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Factors affecting migration kinetics from a generic epoxy-phenolic food can coating system

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ABSTRACT

This study investigated how the properties of a polymeric can coating film, such as thickness and crosslink density as well as the type of migrant, influence the migration kinetics of model migrants in an attempt to better understand, model and control the migration process. Four model migrants were used BADGE (bisphenol A diglycidyl ether), BADGE·H_2O, cyclo-diBADGE and Uvitex OB, that differ in size and polarity. Fatty and aqueous food simulants were used at high temperatures (70–130 °C). The apparent diffusion coefficients were found to decrease with increasing crosslink density, while they increased with increasing film thickness. The apparent activation energy of BADGE and BADGE-related compounds was calculated from the diffusion data and were high, in the range of 250–264 kJ mol^{-1}. The polarity of the simulant and the polarity of the migrant were found to influence migration. The results can be used to improve existing migration models, and thereby help to reduce migration from packaging into food by using safety-by-design approaches in new product development.

1. Introduction

An internal can coating is a thin polymeric film, which is used to prevent corrosion of the metal by the content of the can (food or beverage) and metal pick-up by the food. Typical thermoset polymeric films are crosslinked networks, which are the result of different chemical reactions taking place during the high-temperature 'cure' (i.e. polymerisation). The typical curing temperature for epoxy-phenolic lacquers in industry is 200 °C (Manfredi et al., 2005). The formed three-dimensional networks contain unreacted compounds as well as reaction products, which have the potential to migrate into the foodstuff with which they are in contact. The heat treatment (typically ≥ 121 °C) used to sterilise the can contents enhances such migration (Munguia-Lopez, Gerardo-Lugo, Peralta, Bolumen, & Soto-Valdez, 2005; Simoneau, Theobald, Roncari, Hannaert, & Anklam, 2002).

Migration from packaging materials may change the quality of the foodstuff and may give rise to safety concerns. Many successful efforts have been made to identify migrants from can coatings (Schaefer, Mass, Simat, & Steinhart, 2004; Schaefer & Simat, 2004). Probably the most well-known migrant is bisphenol A diglycidyl ether (BADGE), which is a fluorescent molecule with a molecular weight of 340 g mol^{-1}. BADGE is the reaction product of bisphenol A (BPA) with epichlorohydrin (ECH) and forms an epoxy resin. Epoxy-based can coatings are polymeric networks, which are formed by the pre-polymerisation of epoxy resins and then crosslinked by phenolic or amino resins, etc. Virtually BADGE-free epoxy-based coatings are now available. However, it is not only the starting materials that may migrate from can coatings but also what have become known as the NIAS (not intentionally added substances), including the impurities of the starting substances and the low molecular weight (hence migratable) reaction products - most notably the oligomers.

When migration studies from epoxy-phenolic can coatings are carried out using aqueous foods or food simulants, the migrant BADGE is usually not found in the aqueous food or food simulant due to its rapid hydrolysis to BADGE·H_2O and BADGE·2H_2O (Biles, White, & McNeal, 1999; Mock & Steiner, 1999). Hydrolysis products of BADGE are usually not formed in fatty foods or food simulants, because the lipophilic BADGE partitions strongly into the fat phase and this seems to protect the molecule from hydrolysis even if an aqueous phase is present too. Apart from reactants and reaction products, coatings may also contain

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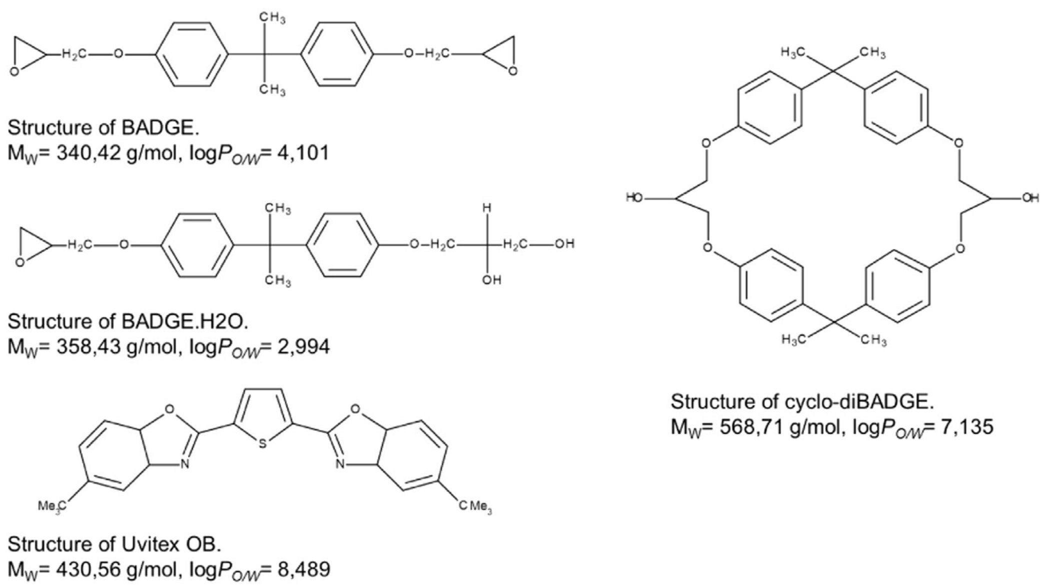

Fig. 1. Structure, molecular weight and log $P_{O/W}$ of BADGE, BADGE·H_2O, Uvitex OB, and cyclo-diBADGE.

additives, which can also migrate into food.

BADGE, BADGE·H_2O and cyclo-diBADGE were used here to study the influence of various parameters on their migration kinetics. Uvitex OB was also used as a model migrant. It is an additive used in the plastics industry as an optical brightener. Important parameters addressed in this study were crosslink density, film thickness, temperature, food simulant, and type of migrant.

The aim of the study was to investigate how the thickness and crosslink density of a polymeric film as well as the type of migrant influenced the migration kinetics of model migrants into fatty and aqueous simulants at high temperatures (70–130 °C), in order to better understand, model and control the migration process.

2. Materials and methods

2.1. Chemicals

Bisphenol A diglycidyl ether (BADGE) (p.a.), Uvitex (OB), Glyceryl tributyrate (98%) and Glyceryl trioctanoate (99%) were purchased from Sigma (Poole, UK). Acetone (analytical grade) was from VWR (Dorset, UK). Acetonitrile (HPLC grade) and Water (HPLC grade) were from Fisher (Loughborough, UK). All other solvents were of HPLC grade (Fisher, Loughborough, UK). Glycerol tributyrate (C4) and glycerol trioctanoate (C8) were from Sigma (Poole, UK). Sunflower oil was purchased from a local supermarket. All chemicals used for lacquer preparation were supplied by Valspar (Grüningen, Switzerland).

2.2. Coating formation

The coating used in this study was a generic epoxy phenolic coating. The raw materials were supplied by Valspar (Grüningen, Switzerland). The composition of the liquid epoxy resin was (wt%): solid epoxy resin = 35.58; glycol ether acetate = 39.00; glycol ether = 20.34 and ester = 5.08. The composition of the generic epoxy phenolic (gEPh) lacquer was (wt%): liquid epoxy resin = 75.82; phenolic resin = 22.07; colouring phenolic resin = 1.7; wetting agent = 0.19; wax additive = 0.11, catalyst = 0.11. The solid epoxy resin was first dissolved in the aromatic solvent, obtaining a liquid epoxy phenolic prepolymer. This prepolymer was checked for absence of any solid epoxy particles, using a grind gauge, before proceeding with the lacquer preparation. The final generic epoxy phenolic lacquer was obtained by mixing the liquid epoxy phenolic prepolymer with the phenolic resins, solvents, as well as a wetting agent, a wax additive and a catalyst. In contrast to the formulations used in industry, the lacquer used for this study was of basic composition and some additives, mainly waxes, were excluded as the coating was not intended for industrial use and a simplified coating composition was desired.

The epoxy phenolic lacquer was applied to industrial tinplate panels (170 × 80 mm, Impress, La Flèche, France) by means of a bar coater, and subsequently cured (polymerised) in an oven (LTE Scientific, Oldham, UK) at 200 °C for 10 min. To minimise heat loss when opened, the oven was insulated with glass wool (covered with aluminium foil), leaving just a narrow slot (5 × 30 cm) for inserting the metal panel. Small strips (15 × 60 mm) for testing were cut from the coated metal panel by using a guillotine before conducting the migration experiments. The one-sided surface area of the samples used for the migration experiments was 9 cm^2.

2.3. Model migrants

In order to facilitate the study of BADGE migration, a generic epoxy-phenolic can coating (gEPh) with deliberately high levels of BADGE was prepared in the laboratory. The amounts of BADGE·H_2O and cyclo-diBADGE present in the final coating were consequently sufficient for the migration experiments. Uvitex OB was added to serve as another model migrant. The structures, molecular weight and the octanol/water partitioning coefficient (log $P_{O/W}$) of the model migrants used in this study are given in Fig. 1. The log $P_{O/W}$ values were calculated using the free software Molispiration (Molinspiration, 2002).

The initial amount of the BADGE and BADGE-related substances differed with the curing conditions. As an example, for standard cure (10 min at 200 °C) the amount in the cured coating was as follows: BADGE = 566 ± 5.6% mg/cm^3; BADGE·H_2O = 201 ± 9.6% mg/cm^3; cyclo-diBADGE = 704 ± 8.1% mg/cm^3; Uvitex OB = 28 ± 4.8% mg/cm^3. The coefficient of variation (CV) was calculated for replicates that did not originate from the same panel (inter-panel deviation).

2.4. Influence of curing time

The standard curing conditions for the gEPh can coating were 10 min at 200 °C. To study the effect of the curing time on the migration of BADGE from the coating into sunflower oil, the curing time was varied from 5 min to 20 min, namely 5, 7, 9, 10, 13, 15, 17 and 20 min at 200 °C.

As the temperature differences across the panel in the oven may affect the cure and, thus the concentration of BADGE and its

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