

Migration behavior of oligomers from BPA-non-intent polyester can coatings under sterilisation conditions

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Introduction

Driven by the discussions on and concerns over Bisphenol A (BPA), alternatives to can coatings based on epoxy resins have been and are being developed, so-called BPA-non-intent lacquers. An important group of these alternatives are polyester based can coatings. The polyesters are usually formed by the reaction of bifunctional carboxylic acids and alcohols [1]. During the polymerization process short chain oligomers can be formed as reaction by-products. They remain in the cured lacquer and potentially migrate into food. The alternative fat simulant 95% ethanol may destroy polyesters by transesterification. It is known that it may cause exaggerated overall migration. Therefore, there is a need to define suitable simulants and migration test conditions for testing of polyester can coatings for food preserves. The simulants shall not resolve the lacquer from the metal plate nor react with the lacquer to form new oligomers neither react with the oligomers and change their structure. The test shall be slightly stronger than migration expected in real foods but not exaggerate migration.

Method

A model polyester-phenol can coating with known composition had been applied onto tin plates at laboratory scale (Fraunhofer IPA, Stuttgart). The plates were extracted with acetonitrile at 40°C for 1d, filtered and analysed with high resolution LC-MS to identify possible migrants and determine their initial concentration in the material. To simulate sterilisation the plates were clamped into metal migration cells and subjected to different food simulants (water, 10% ethanol-, 50% ethanol- and 95% ethanol-with-water mixtures, 2-propanol, isooctane) at 121°C for 30 min in an autoclave. The cells were allowed to cool down, the solvents filtered and analysed with LC-MS. Analyses were conducted using an Acquity UPLC system coupled to a Synapt G2Si (Waters).

Column: Acquity UPLC BEH C18 1,7 µm 2,1x50 mm (Waters)

LC conditions: 0.35 ml/min, solvent A: methanol + 0.1% formic acid, solvent B: water + 0.1% formic acid, from 15% A to 100% A in 8 minutes, keep at 100% for 2 min and then to 15% in 0.1 min and keep at 15% for 3 min

Ionization: ESI positive

Mass range: 50 – 1200 m/z

External standard: cyclic PET trimer (LOQ = 0.1 ng/mL)

Results and Discussion

Cyclic and linear oligomers were identified after extraction with high resolution LC-MS. Identification was performed by accurate mass measurements, evaluation of the mass fragment patterns and correlation of suggested sum formulas with the known ingredients of the polyester and phenol resin. All oligomers could be attributed to components of the polyester consisting of diacid components and dialcohols. Due to the fact that isomeric diacids were used as monomers (terephthalic acid and isophthalic acid) isomeric oligomers were identified as well. They have the same mass but differ in the retention time at the LC separation.

The isomers of three cyclic oligomers which showed high concentrations (0.37 – 9.07 µg/cm²) in the coating material were chosen as model substances to study the migration behavior. The simulants for migration testing of plastic materials isooctane, water, 10% ethanol, 50% ethanol and 95% ethanol as well as additionally 2-propanol were tested. 2-Propanol partially resolves the coating and is therefore not suitable.

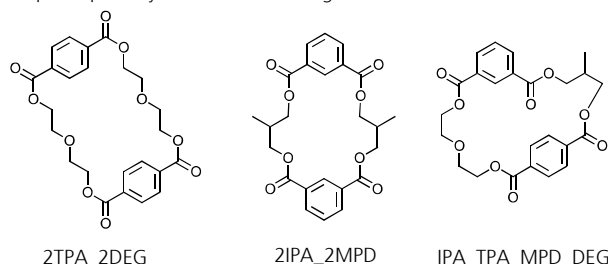


Figure 1: Chemical structures of example oligomers in can coating PE1/PH to study the migration behaviour (TPA – terephthalic acid, IPA – isophthalic acid, DEG – diethyleneglycol, MPD - 2-methyl-1,3-propanediol)

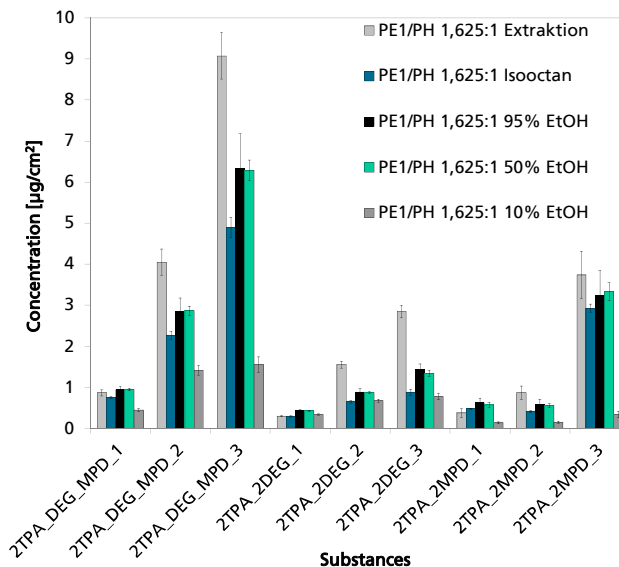


Figure 2: Concentration of model substances in the lacquer PE1/PH extracted by acetonitrile and levels of those substances migrating under sterilisation conditions (121°C, 30 min).

The concentrations of the model substances in the water migrate have been below the limit of detection in most cases.

Migration results per simulants under sterilisation conditions and the initial concentrations of the oligomers in the lacquer are shown in Figure 2. The amount per area of the substances migrating into the food simulants is equal or lower than the initial concentration of the substances in the lacquer. Migration of the tested substances into 50% ethanol and 95% ethanol is similar. Migration into isooctane is somewhat and into 10% ethanol clearly lower than into simulants with a high ethanol content due to worse solubility. This was also shown for a similar lacquer system with different cyclic oligomers (results not presented). Of the oligomers available, approximately 73% are migrating into 95% ethanol food simulant which corresponds to a migration of 1.73 mg/dm².

To monitor formation of new oligomers by hydrolysis and of reaction products with the simulants, masses of theoretically possible molecules were determined and extracted from the LC-MS-chromatograms. Linear molecules resulting from the reaction of the cyclic oligomers with ethanol were detected in the ethanol containing food simulants. Their concentration increased with increasing ethanol content. It still has to be clarified if these linear oligomers arise due to the reaction of the cyclic oligomers with ethanol or if the solvent damages the polymer network and produces more migrateable substances over time.

No reaction or degradation products of the oligomers have been detected in the isooctane migrates and isooctane does not resolve the coating. Hence it might be a good simulant. From theory, solubility of polyester oligomers is expected to be lower in isooctane than in vegetable oil. Whether isooctane is suitable as fat simulant needs to be verified by comparative migration experiments into oil.

Acknowledgements

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References

[1] A. Schaefer, V. A. Ohm, T. J. Simat, Food Addit Contam A 2004, 21, 377-389.

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