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Investigation into the release of nanomaterials from can coatings into food

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ABSTRACT

In this study internal and seam covering coatings as used in food cans were investigated on their potential to release nanomaterials (pigments, fillers) when food is stored and processed (sterilised) within coated cans. Two interior lacquers based on epoxy- and polyester- (with and without bisphenol A) resins and two seam covering coatings were used as lacquer matrices covering typical lacquer formulations. Eight different nanomaterials (four pigments and four fillers) were investigated that are typically used for adjusting colour and enhancing thermal and mechanical stability of the coatings. Aqueous sodium dodecylsulfate surfactant solution showed best suitability to disperse the nanomaterials with sufficient stability. A stable multi-nanomaterial dispersion, containing all eight nanomaterials at the same concentration each, was successfully used to develop an analytical method based on asymmetric flow filed-flow fractionation (AF4) coupled with multi angle laser light scattering (MALLS) detection and inductively coupled plasma mass spectrometry (ICP-MS) that allowed screening for possibly migrating nanomaterials at a limit of detection of 0.5 mg/dm^2. Coated metal plates were brought in contact with the aqueous surfactant solution as alternative food simulant for 2 h at 130 °C (sterilisation) followed by for 10 days at 60 °C (long-term storage). Via AF4/MALLS measurements the release of small oligomeric components from internal coating formulations was detected. However, the particle- and element-specific detection system demonstrated the none-migration of nanomaterials (fillers or pigments) from all test samples.

1. Introduction

Metal based packaging finds application as e.g. closures, lids, tubes, beverage and food cans. Metal food packaging benefits from its high thermal and mechanical stability. In case of canned food, metal based food packaging is the first choice due to its ability to keep the packaging undamaged and tight during sterilisation and long-term storage. Metal cans are produced from metal sheets (e.g. tin, aluminium, certain steel grades) that are usually rolled to cylinders and welded along the side wall (joint or seam). To prevent interactions between the metal and packed food (especially in case of e.g. acidic food) cans need to be lacquered or coated on the inside food contact side. The lacquer protects the metal from electrochemical reactions which may result in corrosion or gas formation (shaping) in the can. Furthermore the coating protects the food from release of metal ions which may cause sensory deterioration or even health related concerns (Oldring & Nehring, 2007). The metal sheets are coated by a liquid lacquer and heat cured before cutting and forming the cylinder or the end parts. After forming the base cylinder, there is a free metal edge at the seam which still needs to be protected. For this powder lacquers are used. In the past mainly epoxy lacquers have been used for can coatings. Due to the critical discussion on Bisphenol A (BPA) which is a starting substance for the epoxy part, more and more alternative lacquers have been developed. An important group of these BPA non-intent lacquers is polyester based. In the lacquer formulation, additives are used to adjust properties of the coating like flexibility, mechanical/thermal stability, barrier effect or colour (Dubbert, Schwirn, Völker, & Aper, 2014; Koleske, Springate, & Brezinski, 2013, Oldring & Nehring, 2007).

The special focus of this study is on pigments and fillers in the lacquers. Pigments are milled down to nanometer size in order to obtain fine dispersability. Others like carbon black or synthetic amorphous silica are produced ab initio as primary particles in the nanosize which are strongly fused together to aggregates and agglomerates (Flörke et al., 2012; Gray & Muranko, 2006; Wang, Gray, Reznek, Mahmud, & Kutsovsky, 2003). As fillers layered silicates are used which may exfoliate to platelets. These pigments and fillers are embraced by the definition of nanomaterials according to Commission Recommendation 2011/696/EU of the European Union (EU, 2011a, 2011b). Due to their high specific surface area, nanomaterials might be more reactive or have different physico-chemical properties than larger structured

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substances. But it is mostly unknown, whether nanomaterials exhibit a toxicological impact at oral exposure e.g. via food with the exception of synthetic amorphous silica (E551) and titanium dioxide (E171) which are used as direct food additives for decades. Due to this gap of knowledge the legislator acts precautious. In plastic materials for food contact, the risk of nanomaterials used as additives must be evaluated on a case-by-case basis. Only nanomaterials which are explicitly approved in their nano-form, are allowed to be used independently if in the direct food contact layer or behind a functional barrier (EU, 2011a, 2011b). Can coatings are not covered by the Plastics Regulation (EU) No. 10/2011 and there is not any specific regulation on the composition of such lacquers with exception of Commission Regulation (EC) No 1895/2005 on the restriction of use of certain epoxy derivatives in materials and articles intended to come into contact with food (EC, 2005). However, Article 3 of Commission Regulation (EC) No 1935/2004, which applies to any food contact material, requires:

> "[…] any material or article intended to come into contact directly or indirectly with food must be sufficiently inert to preclude substances from being transferred to food in quantities large enough to endanger human health or to bring about an unacceptable change in the composition of the food or a deterioration in its organoleptic properties" (EC, 2004).

Risk is the product of hazard (toxicological properties) and exposure. Thus to evaluate the safety of nanomaterials used as additives in can coatings, a feasible way is to investigate whether exposure of the consumer to nanomaterials can occur, i.e. whether the nanomaterials are able to migrate out of the packaging (coating) into food. Within the last years a large number of studies investigating the migration of nanomaterials out of plastic materials into food or food simulants was published and also summarized in several reviews (Duncan & Pillai, 2015; Kuorwel, Cran, Orbell, Buddhadasa, & Bigger, 2015, Störmer, Bott, Kemmer, & Franz, 2017). However, until now the results are mostly not consistent and sometimes even contradictory. Investigating the migration potential of nanomaterials requires suitable analytical techniques and an experimental design that considers the particulate nature of the analyte throughout the experiment. The experimental design of many published migration studies did not allow exclusion of artefact formation and therefore the possibility of false-positive results (Addo Ntim, Thomas, & Noonan, 2016; Noonan, Whelton, Carlander, & Duncan, 2014; Störmer et al., 2017). The conclusion of this comprehensive comparison of the published studies was that nanoparticles which are completely embedded into a plastic polymer are immobilized in the polymer and will not migrate out of the polymer.

Studies on release of nanomaterials from lacquers on metal substrates like can coatings have not yet been published.

The scope of this study was to investigate whether those nanomaterials used as additives in can coatings will migrate into food. Thereby, the study comprised four different pigments, four different fillers and also different lacquers. This way, typical applications of internal as well as seam covering can coatings were considered. Combining asymmetric flow field-flow fractionation (AF4) with a multi angle laser light scattering (MALLS) detector and/or an inductively coupled plasma mass spectrometer (ICP-MS) allows for particle- and element-specific detection of nanomaterials in a suitable food simulant. The lacquers, especially the powder lacquers for seam covering, contained simultaneously several nanomaterials up to six nano-components. In total four pigments and four fillers, i.e. eight nanomaterials were investigated in the study. To handle this multitude of components, a multimethod was developed for simultaneous detection of the nanomaterials using a multi-nanomaterial dispersion as reference for calibration. The aim was to screen the food simulant taken from migration experiments for the presence of any of the respective nanomaterials.

Table 1
Description and composition of the four test-samples investigated in this study.

Application	Sample 1 interior lacquer	Sample 2 interior lacquer	Sample 3 Seam covering lacquer	Sample 4 seam covering lacquer
Lacquer-matrix	Epoxy	Polyester, BPA-n.i.a.	Polyester	Polyester
Film Thickness	200 µm	200 µm	120 µm	120 µm
Pigment	A	A	B	B + C + D
Filler	None	None	A + B + C	A + B + D

2. Materials and methods

2.1. Materials

Within the study four different can coatings (two interior and two seam covering coatings) were investigated which differed in the type of lacquer as well as in the number and amount of pigments and fillers used (Table 1). All can coatings were provided as flat tin plates lacquered with the respective coating formulation. The interior lacquers (provided by Schekolin AG, Liechtenstein) were applied onto laser-cut discs with D = 116 mm using a lab scale coating knife (sample 1 and 2, prepared and provided by Bruchsaler Farbenfabrik GmbH & Co. KG, Germany). For interior coatings two overlying layers of approx. 100 µm each were applied on the discs (total film thickness approx. 200 µm). It should be noted that usually in practice thinner coatings (typically 20 µm and less) are applied. However, coatings of more than 100 µm in thickness were used in this study to exclude formation of rust and to generate are worse-case in sense of higher a nanomaterial loading per test sample area. Seam covering powder lacquers (Schekolin AG, Liechtenstein) were lacquered as single layer of approx. 120 µm on tin plates in A4 format (sample 3 and 4, prepared and provided by Schekolin AG, Liechtenstein). Although the powder lacquers are usually applied as narrow bands on the seam only, full area coated plates were produced in order to enhance the sensitivity of the test. From sample 3 and 4 plates circular test specimens (D = 116 mm) were cut using tin snips. In total, the coated can samples contained eight different nanomaterials (four pigments and four fillers, Table 2) which were additionally provided as powders (Schekolin AG, Liechtenstein). The filler and pigment powders were used to produce reference dispersions for AF4/MALS and ICP-MS measurements. Reference samples without nanomaterials in the coating formulation were available for the interior lacquers sample 1 and sample 2 (Bruchsaler Farbenfabrik GmbH & Co. KG, Germany).

2.2. Preparation of nanomaterial reference dispersions

The scope of the dispersion experiments was to produce a stable multi-nanomaterial reference dispersion that contained all eight nanomaterials in the same concentration ("NM-mix"). An aqueous solution of ultrapure water (TKA Gen Pure, Thermo Scientific, USA) with each 2000 mg/l sodium hexametaphosphate (crystalline, Sigma Aldrich, USA), sodium dodecylsulfate (SDS, ultra-pure, Carl Roth, Germany} and polyvinylpyrrolidone (PVP, 1,3E6 g/mol, Alfa Aesar, USA) was used as dispersant for the preparation of individual stock dispersions first. 0,5 g of the respective nanomaterial were weighed out in 50 ml centrifugal vials and filled with 25 ml of the dispersant. All dispersions were treated with an ultra-sonication tip (Vibra Cell VC50T, Sonics& Materials, USA, 50 W, 20 kHz, 100% output) three times for 15 min successively to break up large agglomerates. During ultra-sonication the dispersions were cooled in an ice bath. At the end the dispersions were quantitatively transferred into 50 ml volumetric flasks, which were filled to the mark with the dispersant solution.

Dispersions prepared this way remained stable at room temperature without any optical change for 24 h. However, after approximately one