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A model study into the migration potential of nanoparticles from plastics nanocomposites for food contact

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ABSTRACT

An experimental study on the migration into food simulants of TiN nanoparticles (NPs) incorporated at three different levels in low density polyethylene (LDPE) films was carried out under severe test conditions. It was shown that within the analytical sensitivity of the applied ICP-MS method no measurable migration of titanium was found at detection limits to 0.09–0.11 $\mu g\,kg^{-1}$ for the food simulants 95% ethanol and iso-octane and 0.24 $\mu g\,kg^{-1}$ for 3% acetic acid. In addition a migration model generally applicable for nanoparticles was established based on an existing migration model for conventional polymer additives to explore into the migration range below the experimentally accessible detection limits. The modeling results indicate that measurable migration may only occur for NPs up to approximately 3.5 nm in diameter but not for larger ones. Overall, the conclusion was drawn that due to the usual size, shape and aggregation of NPs in plastics nanocomposites nanomaterials are immobilized in food contact plastics. Exposure of the consumer to nanomaterials via migration from food contact plastics cannot be expected.

1. Introduction

Food and beverage packaging materials based on plastics have gained increased importance during the last decades which is due to their ease of production, processing and low weight (Brody, Bugusu, Han, Sand, & McHugh, 2008). However, in comparison to other packaging materials like glass or metal, polymeric packaging materials suffer from e.g. lower thermal and mechanical stability, minor gas or vapour barrier and insufficient light protection. Nanotechnology is considered to have the potential to overcome some of these disadvantages of neat polymers leading to a rapid growth of potential nanotechnology applications in the packaging sector (Arora & Padua, 2010; Azeredo, 2009; Sozer & Kokini, 2009). By incorporation of nanomaterials (NMs) such as nanoclays and others into a polymer matrix nanocomposites can be produced with improved properties and enhanced functionalities (Bradley, Castle, & Chaudhry, 2011; Chaudhry et al., 2008; Cushen, Kerry, Morris, Cruz-Romero, & Cummins, 2012; Dallas, Sharma, & Zboril, 2011; Duncan, 2011; Emamifar, Kadivar, Shahedi, & Soleimanian-Zad, 2010; Espitia et al., 2012; Lok et al., 2007; Shi et al., 2014; Silvestre, Duraccio, & Cimmino, 2011; Weiss, Takhistov, & McClements, 2006). As a result an enhanced shelf life of the packed food is expected.

In parallel to this fast technical development in the area of consumer products, an increase in data and knowledge about interactions between NMs and humans via migration from food contact materials is needed. Exposure via oral uptake of NMs by the consumer as a consequence of potential release of

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nanoparticles from NMs containing food packaging materials is still a public concern, wherefore authorities follow in this area strictly the precautionary principle (Cushen et al., 2012; Duncan, 2011; Hatzigrigoriou & Papaspyrides, 2011; Mahalik & Nambiar, 2010; Restuccia et al., 2010; Siegrist, Cousin, Kastenholz, & Wiek, 2007). Within the European Union (EU), as sort of a basic principle, all NMs used for plastic food contact materials (FCMs) must be assessed on a case-by-case basis. In article 9 of the EU Plastics Regulation 10/2011 it reads: ''Substances in nanoform shall only be used if explicitly authorized and mentioned in the specifications in Annex I'' (EC, 2011). Until now titanium nitride (TiN) is the only plastic additive that is approved in nanoform and listed under FCM no. 807 with some specifications and restriction in use in the positive list of the EU Plastics Regulation. Nanosized TiN is used as a so-called reheat additive in the production of bottles made of polyethylene terephthalate (PET). The additive enables a better heat transfer to the polymer during stretching of the PET preforms into final PET bottles. In the PET matrix TiN exists as aggregates and agglomerates with diameters between 100 and 500 nm (EFSA, 2012) consisting of primary spherical particles with a diameter of approximately 20 nm. A safety evaluation of nanoscale TiN was performed by the European Food Safety Authority (EFSA) based on migration measurements on PET bottles with 20 mg kg^{-1} TiN in the polymer and very conservative calculations of the potential migration. It was concluded that no exposure of TiN can be expected under the intended conditions of use (EFSA, 2012). Therefore TiN was included in the positive list with the restriction to be used only in PET bottles at concentrations up to 20 mg kg^{-1}.

Besides the data provided in the EFSA opinion, we are not aware of any other study that focused on the migration of TiN nanoparticles. In general, only little data about the migration of NPs from FCMs to food is published so far. Until now there is no standard or generally recognized methodology available for the sufficiently sensitive and unambiguous detection of NPs migrating out of FCMs. An overview and a more detailed discussion on this issue can be found in our recently published paper on a study dealing with the potential migration of nano silver particles incorporated in polyolefins (Bott, Störmer, & Franz, 2014).

The objective of this study was to carry out a model study on the migration potential of NPs when incorporated in polymers. The intention was to generate data and a working migration model which allows to draw a general conclusion in this still poorly explored question of interest: can NPs migrate from food contact polymers according to Fick's laws of diffusion as known from conventional polymer additives of organic chemical character. A number of pre-considerations are of great importance: (i) the polymer matrix should have high diffusion characteristics to allow any mass transport on NPs in its matrix; (ii) the primary NPs should be small, of spherical structure and chemically be different from usual elements which would allow specific and sensitive analysis for instance via ICP-MS; (iii) the migration tests should be done at different levels of the NPs in the polymer and in a time and temperature dependent approach. From these pre-considerations we concluded on the following study design.

In contrast to the studies referred to in the EFSA opinion we have chosen low density polyethylene (LDPE) as polymer matrix which is generally known to show up the highest diffusion characteristics among usual food contact polymers. TiN was chosen as model NP for the following: the almost spherical structure of primary particles (Guo et al., 2010) facilitates diffusion through a polymer matrix, whereas the aggregated structure of TiN is typical for many other NMs, like carbon black or synthetic amorphous silica, too (Bugnicourt, Galy, Gérard, Boué, & Barthel, 2007; Flörke et al., 2012; ICBA, 2004; Voll & Kleinschmit, 2010). Furthermore, and highly important, by using element specific techniques like inductively coupled plasma mass spectrometry (ICP-MS) migration samples can be analyzed for titanium very specifically and at low detection limits. For migration mechanistic interest the LDPE host polymer was spiked with 3 different levels of TiN NPs to explore whether concentrations dependencies can be found. By using different food simulants in the migration study and severe storage conditions a wide range of practice-oriented applications were covered. For further plausibilisation of the experimental results and in support of the any further generalization of migration prediction also for other NPs/polymer systems the intention was to establish a general NP migration model based on currently recognized diffusion models for conventional polymer additives.

2. Materials and methods

2.1. *LDPE test films*

A TiN dispersion with 8% TiN in white mineral oil was provided by Colormatrix, UK. A TiN-/LDPE masterbatch was produced by compounding the dispersion into a neat LDPE matrix (Lupolen 1806 H, LyondellBasell). LDPE films with three different concentrations of TiN in the polymer (LDPE A, B and C) were extruded using a Collin flat film extruder (Dr. Collin GmbH, Germany). The TiN-/LDPE masterbatch was mixed again with the same LDPE used for the masterbatch and was extruded to films of 60 μm thickness. LDPE blanks without TiN were produced in the same way as reference (LDPE 0). Thus, LDPE films with intended (nominal) concentration of 0 mg kg^{-1} (LDPE 0), 100 mg kg^{-1} (LDPE A), 500 mg kg^{-1} (LDPE B) and 1000 mg kg^{-1} (LDPE C) TiN were produced.

2.2. *Transmission electron microscopy (TEM)*

TEM images of the polymeric films LDPE A and LDPE C were prepared by Innoform GmbH, Germany, to visualize the distribution and size characteristics of the TiN NPs in the polymer. For sample preparation the polymeric films were subjected to cryo-ultra-thin-sectioning using a diamond knife.

2.3. *Inductively coupled plasma mass spectrometry (ICP-MS)*

The amount of titanium in migration samples and LDPE films (LDPE A, B, C) was determined using a 7700 series ICP-MS (Agilent Technologies, USA). The setup of the ICP-MS is summarized in Table 1. The ICP-MS was calibrated using