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Review

Critical review of the migration potential of nanoparticles in food contact plastics

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ABSTRACT

Background: The development of applications using nanomaterials is accompanied by safety concerns due to gaps in understanding the toxicology. In case of incorporation in food contact polymers, the first step to consumer exposure is the transfer of nanomaterials from the polymer to the food. Thus, in order to evaluate the risk the key questions are whether nanoparticles can be released from food contact polymers and under which conditions.

Scope and Approach: This article critically reviews the published nanomaterial migration studies which are partly contradictory. The influence of analytical techniques and the experimental design on the results are discussed. Theoretical approaches by mathematical modelling are addressed. Furthermore, a short overview on nanomaterial applications for food contact materials and on the regulatory situation in Europe and USA is given.

Key findings and conclusions: Distinguishing between particle release and migration of dissolved ions is crucial for proper interpretation of migration results. Nanosilver which is the mostly investigated species, and other metals are easily oxidized to ions but can re-form nanoparticles at slightly reductive conditions, e.g. at sample preparation, pretending particle migration. At cutting edges the particles may be released due to weak binding to the surface. Nanoparticles which are completely encapsulated in the host polymer matrix do not have a potential to migrate into food. Thus, consumers will not be exposed to nanoparticles from food contact polymers when those are completely embedded in polymer and the contact surface is not altered by mechanical surface stress during application.

1. Introduction

Nanotechnology has arrived in many ordinary consumer products and in food contact polymers in the last two decades due to the potential that nanoadditives can improve certain properties of neat polymers or introduce new functionalities (Mihindukulasuriya & Lim, 2014). This development was paralleled over the last few years by public safety concerns about nanomaterials (NMs) in general and for consumer products particularly. This was substantiated by the fact that NMs may have different physical and chemical properties compared to conventional bulk material and thus may have different and so far not well understood toxicological properties (EASAC & JRC, 2011).

It is well known that the toxicological risk for humans from any substance including NMs is always a combination of the substance's hazard and its exposure to the consumer. For the exposure via the oral route it makes a crucial difference if the nanomaterial (NM) is a direct food additive or if used in a food contact material (FCM) from where it first needs to be released into food. Therefore, one of the main conclusions of the JRC-EASAC report (EASAC & JRC, 2011) is to distinguish between embedded and free NMs.

NMs used as nanoadditives in polymers for food packaging or kitchenware applications are usually incorporated into the polymer matrix and can be considered as embedded. The crucial question for which so far not always concurrent answers have been reported and published is whether nanoparticles from these nanoadditives will be able to move within the polymer nanocomposites (PNCs) to the food contact surface and be released from there into the food. Basically, this could be migration via Fick'ian diffusion as with conventional polymer additives or other material stress based mechanisms such as degradation of the polymer matrix by mechanical abrasion, material fatigue, UV exposure, hydrolysis or swelling interactions (Noonan, Whelton, Carlander, & Duncan, 2014). Purely chemical release can also occur via dissolution of

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NMs into ionic species in the polymer followed by release of ions into the food. Finally, for completeness reasons, nanolayers on top of polymer surfaces may desorb nanoparticulate fragments after mechanical stress and due to weak bonding forces (Duncan & Pillai, 2015; Noonan et al., 2014).

Numerous publications appeared in the last years dealing with the question of the ability of nanoparticles to migrate from PNCs. In 2008 a semi-theoretical approach was published by Simon et al. (Simon, Chaudhry, & Bakos, 2008). Since then the number of publications of migration studies on PNCs has largely increased. However, the reported results and conclusions were not always in agreement and, even worse, often contradictory.

The aim of this review is (i) to summarize the published state of knowledge of NMs migration out of PNCs including analytical aspects and migration modelling approaches and (ii) to critically assess the outcome of these studies to allow drawing conclusions concerning the potential of NMs to migrate out of plastics FCMs. In addition, to set the scene, the other objective is first to provide a short overview of current regulatory issues and implications and to summarize examples of most common applications of nanotechnology used for food packaging on the market versus current legislation.

2. Overview definitions of NMs and legal frameworks for food contact applications

Several national and international standardization bodies, organisations, and authorities have proposed definitions for the term 'NM' and released terminology documents for nanotechnology. A broad overview of existing definitions can be found in the Joint Research Center (JRC) Reference Report EUR 24 403 EN (Lövestam et al., 2010).

In the area of FCMs a comprehensive science-based definition of NMs was introduced in 2011 by the EU Commission Recommendation 2011/696/EU "on the definition of NM" (EU, 2011a). This Recommendation defines 'NM' as "a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm–100 nm". However, in specific cases of concern the threshold of 50% may be replaced by a lower figure between 1% and 50%. This definition is intended to be used as a reference for determining and legally clarifying whether a material should be considered as a 'NM' for legislative and policy purposes in the European Union. Most importantly, this definition of the term 'NM' in EU legislation shall be "based solely on the size of the constituent particles of a material, without regard to hazard or risk".

European Framework Regulation (EC) No 1935/2004, which is laying down the general principles for any material or article intended to come into contact with food, did not yet address explicitly the use of nanotechnology related to such FCMs. However, the general requirements set out in its Article 3 apply to any kind of FCM and, consistently, includes also materials manufactured with and containing 'substances in nanoform'. 'NMs' are specifically addressed in the European Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food (EU, 2011b). The logic is: Since NMs may have different physico-chemical properties and therefore toxicological profiles than larger structured substances (recital (23)), it is clarified that substances in nanoform may only be used if explicitly authorized and mentioned in the specifications in Annex I of the Plastics Regulation (Article 9). In other words: an authorisation of a substance which is based on the risk assessment of the conventional bulk material does not cover its use at nanoparticulate size. According to Preamble 27 risk assessment of engineered nanoparticles has to be performed on a case-by-case basis. As a consequence, 'substances in nanoform' are, besides substances classified as carcinogenic, mutagenic, or toxic for reproduction (CMR substances), explicitly excluded from the functional barrier concept (Article 13, paragraph 4 (b)). This paragraph allows to manufacture a plastic layer with substances *not* listed in the Union list if this layer in a multilayer material is not in direct contact with food and separated by a functional barrier, provided that the migration of such non-approved substances is not detectable at a detection limit of 0.01 mg/kg food (or food simulant). Such an exclusion of 'substances in nanoform' is also defined in the European Regulation (EC) No 450/2009 on active and intelligent materials and articles (EU, 2009). Whereas EU Regulation No. 10/2011 refers generally to 'substances in nanoform', EC Regulation No 450/2009 defines them more specifically as "substances deliberately engineered to particle size which exhibit functional physical and chemical properties that significantly differ from those at a larger scale" which, again, are not covered by the functional barrier concept (Article 5, paragraph 2(c)(ii)). Interestingly, this description of 'nanoparticles' differs distinctly from the solely size related definition of EU Recommendation 2011/696/EU. Finally: The legal assessment of 'nanosubstances' not included in the Union list such as colorants and aids to polymerisation (such as catalysts) is currently unclear.

The US-American Food and Drug Administration (FDA) has not established specific regulations for the use of 'NMs' in food contact applications. Also, there are no *regulatory* definitions of "nanotechnology," "NM," "nanoscale," or other related terms, but a reference is given to the term 'nanometer scale' to any particle between 1 nm and 1 μm in FDA's 'Guidance to industry assessing the effects of significant manufacturing process changes' (FDA, 2014a). This document is reflecting FDA's current thinking on certain issues related to the use of nanotechnology in FDA-regulated products such as food contact substances. Regarding the existing legislation in 21 Code of Federal Regulations (21 CFR), there are no specifications laid down relating to particle size, size distributions and morphology of authorized (indirect) food additives or Generally Recognised as Safe (GRAS) substances. However, according to current FDA perspective as described in the 'Guidance for Industry' (FDA, 2014a), this does not mean that the nanoscale version of a substance listed in the existing legislation is also (automatically) compliant. In contrast, FDA points out that a significant change in the manufacturing process employing nanotechnology may have an impact on the identity, safety and the regulatory status of a food substance and therefore concluded that "when a food substance is manufactured to include a particle size distribution shifted more fully into the nanometer range, safety assessments should be based on data relevant to the nanometer version of the food substance" (FDA, 2014a). Furthermore, FDA issued an additional guidance document for industry entitled "Considering Whether an FDA-Regulated Product Involves the Application of Nanotechnology" (FDA, 2014b). FDA intends to apply the considerations laid down in this guidance document broadly to all FDA-regulated products, including food substances.

3. Nanocoatings in food contact applications

Flexible films and bottles based on polymeric substrates combined with very thin inorganic layers deposited by vacuum coating are commonly used as packaging materials due to their high oxygen and aroma barrier properties. While aluminium foil and aluminium-metallization used to be the material of choice so far, at present new materials are used more frequently. For instance polyester (PET) films and oriented polyamide (OPA) films are often coated with ceramic barrier layers such as aluminium oxide (AlOx)