

Studies on the migration of titanium nitride nanoparticles in polymers

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Introduction

With the new Plastics Regulation 10/2011, all nanoparticles and their aggregates or agglomerates need to be subjected to separate risk assessments when used directly in a food contact layer but also when applied behind a functional barrier. Only very few data exist on transport processes of nanoparticles in polymers and their migration into foods or simulants. For a risk assessment of nanoparticles used in food contact materials the knowledge on the possible exposure of the consumer, i.e. on the possible amount of migration is a prerequisite. The objective of this study was to explore if titanium nitride (TiN) nanoparticles have a potential to migrate from food packaging polymers when in contact with food simulants. For this kinetic migration tests were performed using polyethylene terephthalate (PET) bottles and low density polyethylene (LDPE) films with incorporated TiN nanomaterial. LDPE is considered to be a worse-case matrix with regard to mobility of migrants. Asymmetric flow field-flow fractionation (AF4) and inductively coupled plasma mass spectrometry (ICP-MS) were used for the detection and characterisation of the nanomaterial.

Materials and Methods

For migration study ready-made PET bottles with a content of 50 ppm TiN nanomaterial were provided by the producer. The same TiN nanomaterial was introduced by extrusion into LDPE films in several concentration levels (0 ppm, 100 ppm, 500 ppm and 1000 ppm). The nanoparticles in the PET bottles and the LDPE films were characterised by transmission electron microscopy (TEM). For migration experiments the PET bottles were stored for 24 hours at 100 °C in the classical simulant 3% acetic acid and 24 hours at 78 °C in the alternative fat simulant 95% ethanol. Migration experiments on the LDPE films were done into the classical simulant 3% acetic acid and the alternative fat simulants isooctane and 95% ethanol. Additionally aqueous solutions with additives to stabilize nanoparticle dispersions were tested as simulants. For this a 0.2% NovaChem (mixture of surfactants, Postnova) solution was prepared. Migration of particles was determined by element specific inductively coupled plasma mass spectrometry (ICP-MS).

Results

The TEM measurements of both the PET bottles and the LDPE films showed that the TiN particles were distributed homogeneously in the polymer. At a higher resolution of the TEM images (Figure 1) single aggregates of TiN can be seen. The observed aggregates were mainly of the size of about 100 nm to 500 nm, whereby the aggregates consist of primary particles of about 20 nm. At all TEM images no isolated primary particles but only aggregates of the TiN nanomaterial could be found.

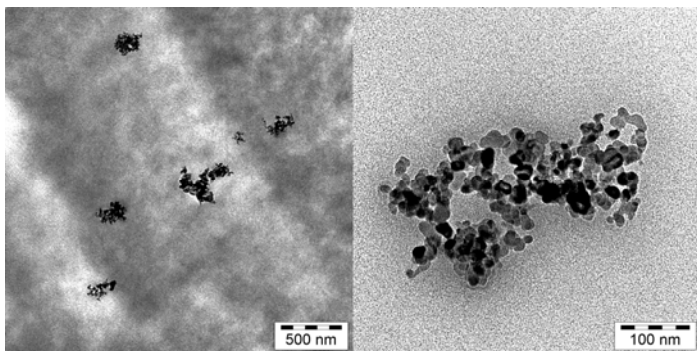


Figure 1: TEM image of TiN nanomaterial in LDPE

Element specific ICP-MS measurements of the PET bottles migration samples showed that in case of 3% acetic acid about 11.8 ng dm⁻² titanium migrated from the PET bottles with 50 ppm TiN nanomaterial and 11.6 ng dm⁻² from the PET reference bottles (Figure 2). At a detection limit of 5 µg l⁻¹ no titanium could be detected in the 3% acetic acid blank. With a detected amount of 0.12 ng dm⁻² titanium for both the PET bottles with 50 ppm TiN and the PET reference bottle, no difference could be found in 95% ethanol.

ICP-MS measurements of the LDPE films migration samples showed that at a detection limit of 15 ng dm⁻² no titanium was detectable in the 95% ethanol, isooctane and the 0.2% Novachem samples. Only in the case of 3% acetic acid titanium was detectable in the migration solutions but in the same concentrations as the blanks.

After a storage of 10 days at 60 °C (accelerated test for long term storage) the measurement of the samples showed a amount of titanium of about 22-27 ng dm⁻² (Figure 3). The averaged content of titanium in the LDPE blank was about 24 ng dm⁻², the 3% acetic acid blank was about 25 ng dm⁻². Thus a titanium migration from the TiN in the LDPE was not detectable.

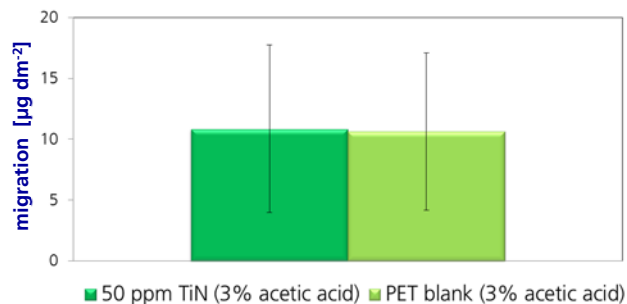


Figure 2: Detected amount of titanium in the 3% acetic acid PET migration samples after 24 hours at 100 °C

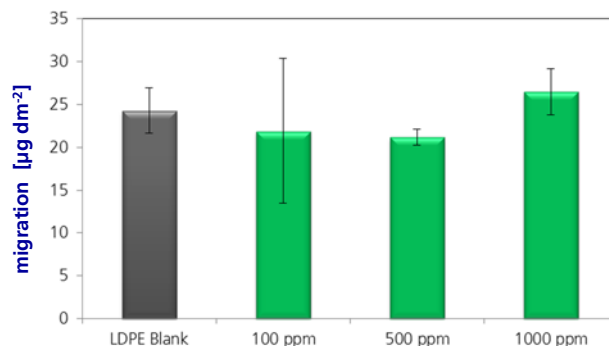


Figure 3: Detected amount of titanium in the 3% acetic acid LDPE migration samples after 10 days at 60 °C

Discussion

The migration of substances from polymer is depending on the mobility of the substance in the polymer matrix. Thus the size of a substance is a crucial parameter, i.e. smaller substances can migrate much faster than bigger ones. The TEM measurements of the polymer films showed, that the TiN nanomaterial indeed consists of primary particles with an average size of about 20 nm, but these primary particles could not be found isolated. Instead the TiN nanomaterial was found as aggregates of an average size of 100 nm to 500 nm. At this size only a very low mobility of the substance in the polymer matrix can be expected. This finding is also supported by other studies (e.g. nanosilver), where the nanomaterial existed partially as primary particles in the polymer, but still no migration of particles could be detected. The performed ICP-MS measurements confirm these findings. 3% acetic acid was the only simulant where titanium could be detected. No difference between the migration samples of the PET bottles with and without TiN could be found. The kinetic migration study on the LDPE samples showed a similar result, where only in the samples, where 3% acetic acid was used as simulant, titanium could be found. This simulant is known to be a strong solvent for inorganic material and also the titanium concentration of the solvent and polymer blank is rather indicating a prior contamination of the simulant than the migration of TiN.

Acknowledgement

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