Size-fractionation and characterisation of nanoparticles used in food packaging by Asymmetric Flow Field-Flow Fractionation (AF4) coupled with a Multi-angle Light Scattering detector (MALS)

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Introduction

Nanoparticles (NP) are increasingly intended to be used in the food packing sector with the intention to improve certain properties of the packing material, e.g. mechanical and thermal performance, barrier properties and to develop active or intelligent packaging applications. Besides these well-known beneficial properties of NP in food packaging, the question to which extend the consumer would be exposed by migration of NP from food packaging is largely unknown.
The objective of this study was to establish a method for the measurement of NP in food simulants to be obtained from migration tests. In a first step, asymmetric flow field-flow fractionation (AF4) was coupled online to a multi-angle light scattering detector (MALS) to develop a method to fractionate and to characterise NP that find application in food packaging. In a second step, migration experiments on NP containing packaging polymers in contact with food simulants were performed to explore whether AF4/MALS is a suitable technique for the detection and separation of polymeric matrix components from possibly migrated NP. Due to the principles of the AF4 technique a separation of polymer matrix components versus NP according to their different sizes was possible.

Principles of AF4 separation

The asymmetric flow field-flow fractionation (AF4) is a separation technique similar to chromatography. The most relevant difference to chromatography is the separation of particles without the usage of a stationary phase. Instead, the AF4 system is equipped with a very thin ribbon-like channel, which is perfused solely by the particular solvent, resulting in a laminar flow with parabolic flow profile. In AF4 the separation force is generated by a second flow profile, called cross flow, which is perpendicular to the laminar flow. The AF4 consists of a thin channel with a solid block at the top and a membrane at the bottom of the channel. The crossflow is generated by evacuating solvent out of the channel through the membrane. In contrast to this separation force the diffusion of particles takes effect in contrary direction. Since the diffusion is depending on the particle size, particles of different sizes are located at different levels in the channel. Smaller particles with higher diffusion are located higher in the channel and are transported after the focussing phase with higher flow velocity in the parabolic flow profile than larger particles. Those have a lower diffusion and are located at lower levels in channel. The larger particles are transported then with lower flow velocity in the flow profile of the channel and elute later than smaller particles (Figure 1). In general AF4 can be used to separate particles from about one nanometer to several micrometers [1].

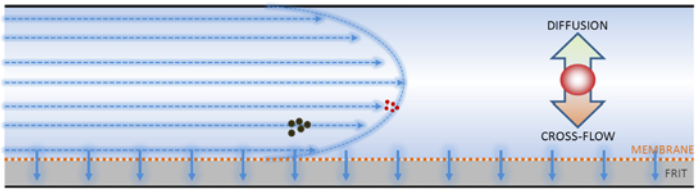

Figure 1: Scheme of the separation of particles in an AF4 channel

MALS detection

According to the theory of AF4 the determination of the particle size by the elution time is only accurate for ideal spherical particles. Non-spherical particles and effects like particle aggregation or interactions with the membrane will affect the retention of the particles and the calculation of particle sizes according to the AF4 theory will only lead to equivalent spherical diameters (stokes diameter). For an exact determination of particle sizes and particle size distributions of a more complex sample a suitable detection technique is necessary. The combination of AF4 with a light scattering detector has been established as a reliable method for the separation and characterisation of particles of different sizes. For this study a multi-angle light scattering detector was coupled online to a AF4 system.
The basic principle of size detection by MALS is static light scattering (SLS) [2]. Laser light is beamed through the detection cell. The particles in the fluid scatter this light in various angles. The scattered light intensity is determined by averaging the fluctuating intensity at a given angle over the measurement period. By the use of several detectors (MALS) the angular dependence of the averaged scattered intensities can be measured. Then, by the knowledge of the angular dependence of the scattered light the size of the particle can be calculated. However the detection of particles by MALS is not specific.

When the detector is used for migration study of nanoparticles used in food packaging it does not differentiate between different types of nanoparticles, polymer chains or other particles. Thus the polymer chains and other interfering compounds from the migration solutions need to be separated by the AF4 method and by optimisation of the flow parameters (Figure 3). If this is not possible the system must be coupled with other detectors, or other techniques must be used. The setup of the AF4 system used for the separation and characterisation of nanoparticles used in food packaging is shown below (Figure 2). In addition to the MALS-detector different concentration detectors (RI-/UV-detector) and a fraction collector were installed. In a first step, it is then possible to separate a sample into fractions of different sizes (AF4) and to characterise them by their particle size distribution (MALS). After a successful separation, individual peaks of the fractogramm can be collected and analysed by element specific techniques like inductively coupled plasma mass spectrometry (ICP-MS). Thus, a capable method is obtained to separate, characterise and identify a broad range of nanoparticles used in food packaging.

Figure 2: AF4 unit: solvent organizer (A), solvent degasser (B), tip-pump (C), focus-pump (D), crossflow-pump (E), autosampler (F), channel with oven (G), MALS detector (H), RI detector (I), UV detector (J), fraction collector (K)

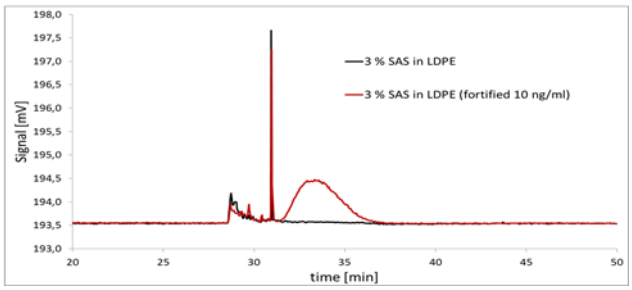

Figure 3: Separation of hydophobised synthetic amorphous silica (SAS) nanoparticles from polymeric components of a fortified migration sample versus a pure LDPE sample.

References

[1] J.C. Giddings, Science, **1993**, *260*, 1456-1464. [2] S. Podzimek, Light Scattering, Size Exclusion Chromatography and Asymmetric Flow Field Flow Fractionation, Wiley **2011**, ISBN 978-0-470-38617-0. [3] M. Bouby et al, Analytical and Bioanalytical Chemistry, **2008**, *392*, 1447–1457.

Acknowledgement

This work was supported by the Bavarian State Ministry of Environment and Public Health within the project 'LENA' on Nanotechnology related Food Safety coordinated by the Bavarian Authority for Public Health and Food Safety (LGL).

Fraunhofer IVV

Poster presentation at the 5th international Symposium on Food Packaging, 14-16 November 2012, Berlin