

# Migration potential of nanoscale silver particles in food contact polyolefins

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## Introduction

Silver nanoparticles (SNP) may be used in active food packaging polymers with the intention to enhance the shelf life of the food [1]. The underlying effect is related to the release of silver ( $\text{Ag}^0$ ) from the surface of the SNP followed by oxidation to antimicrobial active silver ions ( $\text{Ag}^+$ ) [2]. The objective of this study was to explore if SNP have a potential to migrate from food packaging polymers when in contact with food simulants. For this kinetic migration tests were performed using low density polyethylene (LDPE) films with different concentrations of incorporated SNP. 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) are known as a capable method for the detection and characterisation of silver and SNP [3].

## Materials and Methods

For migration study LDPE-films with different contents of silver were used. The masterbatch ROMBEST AM 6500NANO (Romcolor, Romania), which contains 6500 ppm nanosilver of the size range 20-100 nm, and LDPE (Lupolen 1806H) were extruded to films with 0 ppm, 50 ppm, 150 ppm and 250 ppm nanosilver, and 60  $\mu\text{m}$  thickness. The migration tests were performed under different contact conditions to simulate realistic to long-term storage applications using 3% acetic acid, 10% ethanol, 95% ethanol and isooctane as food simulants. The content of total silver ( $\text{Ag}^0$  and  $\text{Ag}^+$ ) in the migration solution was determined by inductively coupled plasma mass spectrometry (ICP-MS). By transmission electron microscopy (TEM) the distribution of SNP in the polymer and their particle sizes in relation to the nominal values was verified. Tests on the stability of SNP were performed using the "AF2000MT series" asymmetric flow field-flow fractionation (AF4) by Postnova, Germany, equipped with a 10 kDa RC membrane. The membrane of the AF4 system was chosen that nanoscale silver cannot pass the channel membrane, whereas the ionic silver is washed out of the channel during the run. For this purpose a 10 nm SNP standard (PL-Ag-S10-1mg, PlasmaChem, Germany) was diluted to 1 ppm with ultrapure water and 3% acetic acid, respectively. Those samples were measured by AF4 directly after preparation of the sample and again after storage for 24 hours at room temperature.

## Results

TEM measurements showed that the SNP were distributed homogeneously in the polymer. The averaged found particle sizes were about 20 nm to 100 nm. The ICP-MS measurements of the migration solutions showed that silver was not detectable in isooctane and 95% ethanol (detection limit 15  $\text{ng dm}^{-2}$ ). Traces of silver were found in 10% ethanol and markable migration in 3% acetic acid (Fig. 1). After storage of 10 days at 60 °C (accelerated test for long term storage) the measurement of the samples with the highest content of SNP (250 ppm) showed a migrated amount of silver of about 760  $\text{ng dm}^{-2}$  in 3% acetic acid and 35  $\text{ng dm}^{-2}$  in 10% ethanol. The migration tests in 3% acetic acid in contact with the samples of different SNP concentrations in the polymer, showed an increasing concentration of migrated silver with an increased SNP concentration in the polymer by ICP-MS.

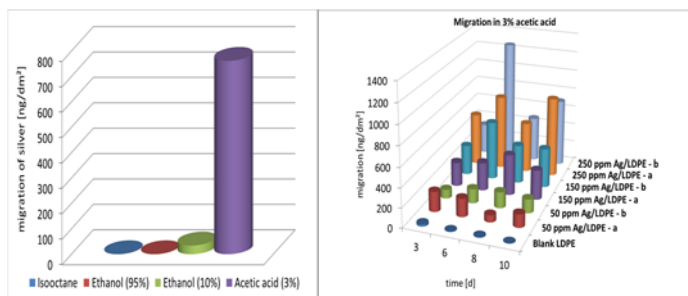


Figure 1: Amount of migrated silver in different food simulants (left); time and concentration dependent migration of silver in 3% acetic acid (right)

By ICP-MS measurements it is not possible to differentiate between elemental silver, silver ions or particular silver. The sensitivity of the AF4 method was not high enough to determine silver particles directly in the migration solutions. Therefore tests on the dispersion stability of SNP were performed by AF4 (Figure 2).

Freshly prepared 1 ppm dispersion in water delivered a clear signal. After 24 hours storage of the dispersion at room temperature, SNP in water still caused a clear but somewhat smaller signal. In the same way 1 ppm SNP dispersed in 3% acetic acid was investigated. After the injection of the freshly prepared dispersion in 3% acetic acid, SNP caused a signal in the AF4 similar to the signal caused by SNP in water. After storage of the dispersion for 24 hours, no signal could be obtained anymore at the whole AF4 run, i.e. the silver nanoparticles have been dissolved via oxidation to  $\text{Ag}^+$  ions.

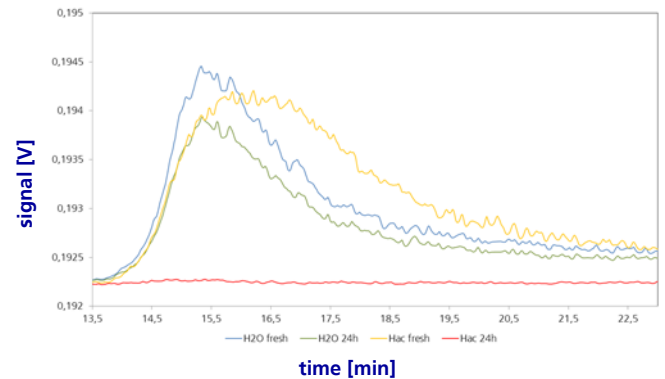


Figure 2: Stability of aqueous and 3% acetic acid SNP dispersions

## Discussion

It is well known that colloidal dispersions of silver release  $\text{Ag}^+$  ions from the surface of the silver particles. This effect is e.g. utilised in drinking water sterilisation. 3% Acetic acid accelerates this oxidation of the silver on the particle surface so that the silver particles were completely dissolved within 24 h at room temperature. We did not measure this kinetically, however, from the quick discoloration of the initially yellow dispersion into a colourless liquid one can assume that this process is much quicker. In 95% ethanol and isooctane the silver nanoparticles remain unchanged. However, migration of silver cannot be detected there. The high silver concentration in 3% acetic acid after migration contact can only be explained by migration of silver ions. The small silver ions (effective ion radius  $\text{Ag}^+$  0.115 nm [4]) diffuse in the polymer much faster than the SNP particles of at least 10 nm. Mechanistically this  $\text{Ag}^+$  migration is enhanced by the penetration of the small acetic acid molecules into the LDPE film. This leads already in the polymer to  $\text{Ag}^+$  formation from the silver particles followed by acetic acid mediated diffusion of the silver ions. The small amount of silver found in 10% ethanol can also be explained by dissolution of  $\text{Ag}^+$  from the silver nanoparticles present at or very close to the surface of the film. The SNP itself remain in the film and the surface. This can be deduced from the finding that silver was neither found in 95% ethanol although the solubility or ability to disperse would have been sufficient nor in isooctane which is known to be very aggressive to LDPE by swelling the polymer. From a migration theoretical view the SNP of at least 10 nm size cannot move anymore at the applied severe test temperatures at a measurable speed in a polymer and therefore are not expected to migrate out of the film. This is supported by other studies with other nanoparticles (e.g. TiN). In conclusion, not the silver particles themselves but dissolved silver ions only are released from the polymer which is the reason for the intended antimicrobial effect of polymers with incorporated silver nanoparticles.

## References

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