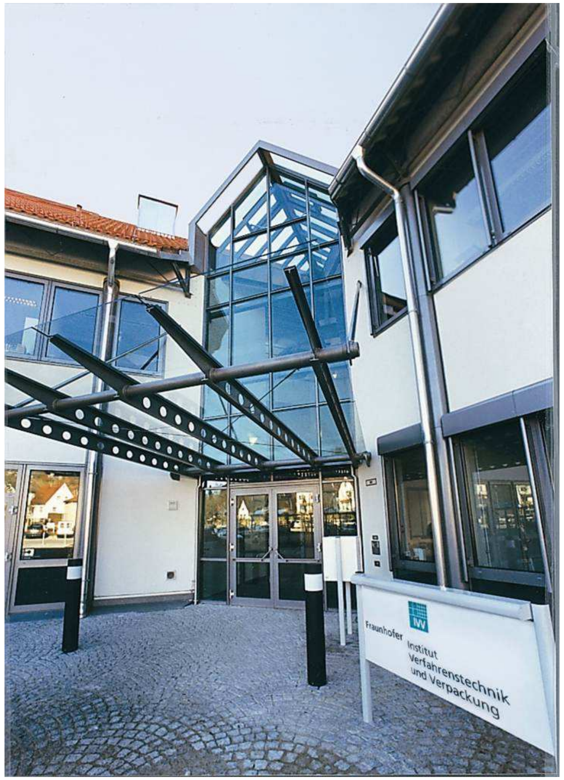


Studies on the potential of nano-particles to migrate from polymer nanocomposites for food contact

Roland Franz
Fraunhofer IVV, Freising, Germany

QEEN Workshop
U.S. National Nanotechnology Initiative
Washington DC, 7-8 July 2015

http://www.ivv.fraunhofer.de

Migration potential of nano-particles from food contact polymers

Titanium nitride (TiN) in PET beverage bottles – a very consumer relevant example of food contact applications

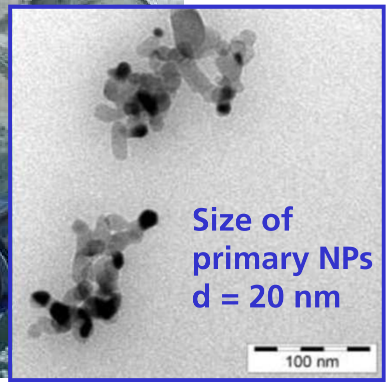
Technical function:

'Reheat additive' - improves thermal properties, increase of production lots

Preforms

blow- moulding

TEM image



⇒ The challenging question:

Can NPs migrate from FC polymers?

Can NPs be released from FC materials?

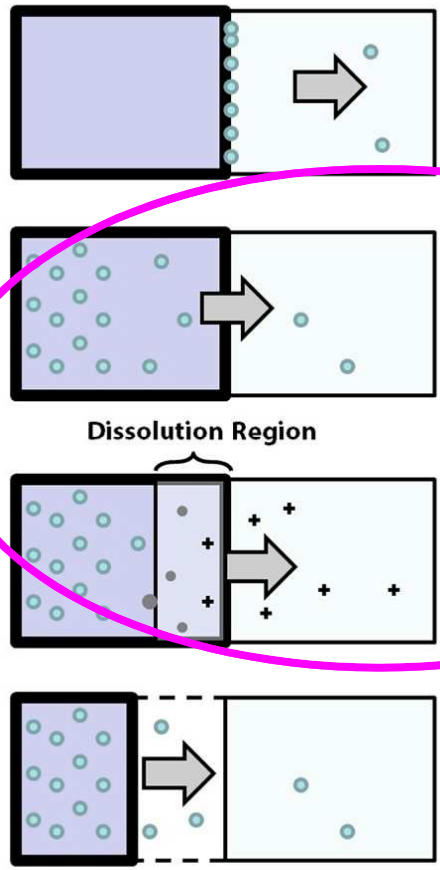
Principal NP release mechanisms

DESORPTION: Weak bonding to surface
- Agitation
- Surfactants / detergents
- pH
- Temperature

DIFFUSION: Migration to low concentration
- Concentration gradient
- Temperature, humidity
- Size, shape, and surface
- Polymer properties

DISSOLUTION: Ions released into product
- pH
- Ionic strength
- Size and shape
- Concentration

DEGRADATION of MATRIX: Loss of polymer
- Mechanical abrasion
- UV Exposure
- Material fatigue
- Hydrolysis / swelling



Separate issue

Focus today

related but separate issue

Figure from: Timothy V. Duncan & Karthik Pillai; Release of Engineered Nanomaterials from Polymer Nanocomposites: Diffusion, Dissolution, and Desorption; ACS Appl. Mater. Interfaces 2015, 7, 2−19.0

Further Agenda

- **Overview of our project studies on the migration potential of ‚nano additives‘ from food contact plastics**
- **Some representative experimental data and analytical methods**
- **Estimation of nanoparticle migration from polymers by migration modeling**
- **Conclusions**

Overview of our experimental model studies

We did a series of experimental studies (migration tests and other) using LDPE polymer (high diffusion properties, worst case matrix) and PS (only for Carbon Black) containing 'nano additives' at various concentrations:

- **Nano-sized titanium nitride, TiN**
  (EU limit 20 ppm in PET)
- **Nano silver**
  (has been used in numerous studies)
- **Carbon black**
  (EU limit 2.5% in polymer)
- **Synthetic amorphous silica**
  (EU limit: no restriction)
- **Laponite**
  (a very small (worst-case) nanoclay)

Data already published (TiN, Nano silver, Carbon black)

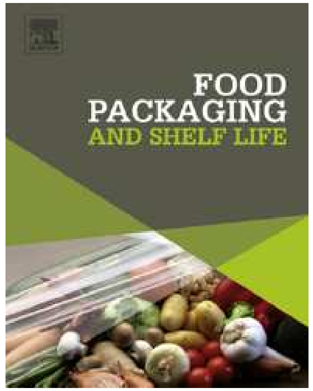
Publications in preparation (Synthetic amorphous silica, Laponite)

3 Publications on the results so far (3 more in the pipeline)

1) **Bott, J.; Störmer, A. and Franz, R.: 'A Comprehensive Study into the Migration Potential of Nano Silver Particles from Food Contact Polyolefins. In Chemistry of Food and Food Contact Materials: From Production to Plate'; Benvenuto, M. A., Ahuja, S., Duncan, T. V., Noonan, G., Roberts-Kirchhoff, E., (Eds.); ACS Symposium Series 1159: 51 - 70; American Chemical Society: Washington, DC, 2014. DOI: 10.1021/bk-2014-1159.ch005.**

2) Bott J., Stoermer A. and Franz R.: Investigation into the migration of nanoparticles from plastic packaging materials containing carbon black into foodstuffs. Food Additiv. Contam. Vol. 31 (10), 1769–1782 (2014). DOI: 10.1080/19440049.2014.952786.

3) **Bott J, Störmer A and Franz R., A model study into the migration potential of nanoparticles from plastics nanocomposites for food contact. Food Packaging and Shelf Life 2(2) 73-80 (2014). DOI: 10.1016/j.fpsl.2014.08.001.**



Model system: nano silver in LDPE

Inhouse production of 3 different LDPE films (100 µm) with nano silver at levels of …..

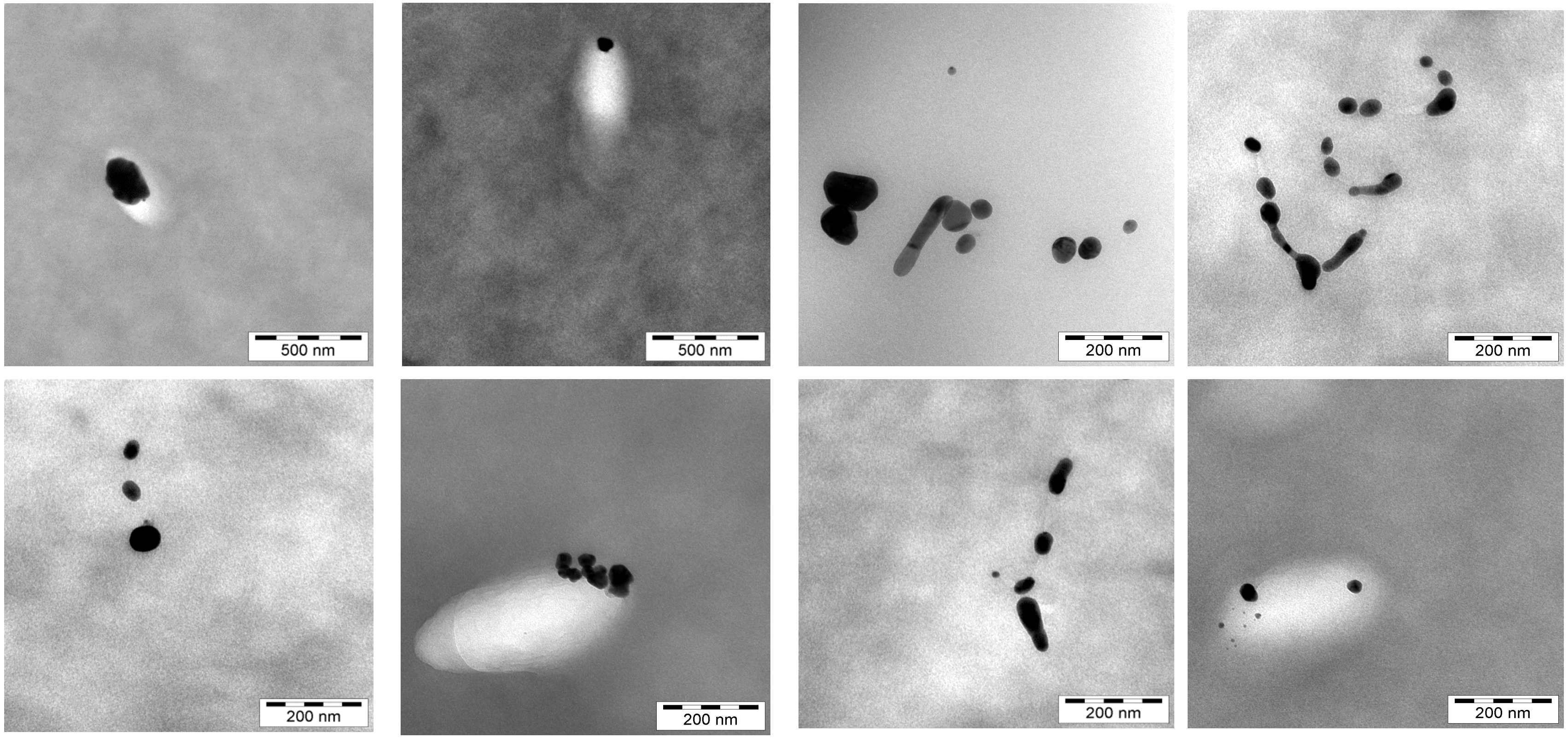
….0 ppm (blank), 50 ppm, 185 ppm and 250 ppm

…using a commercial masterbatch of nano Ag in LDPE

Model system: nano silver in LDPE

TEM images of the worst-case test material:

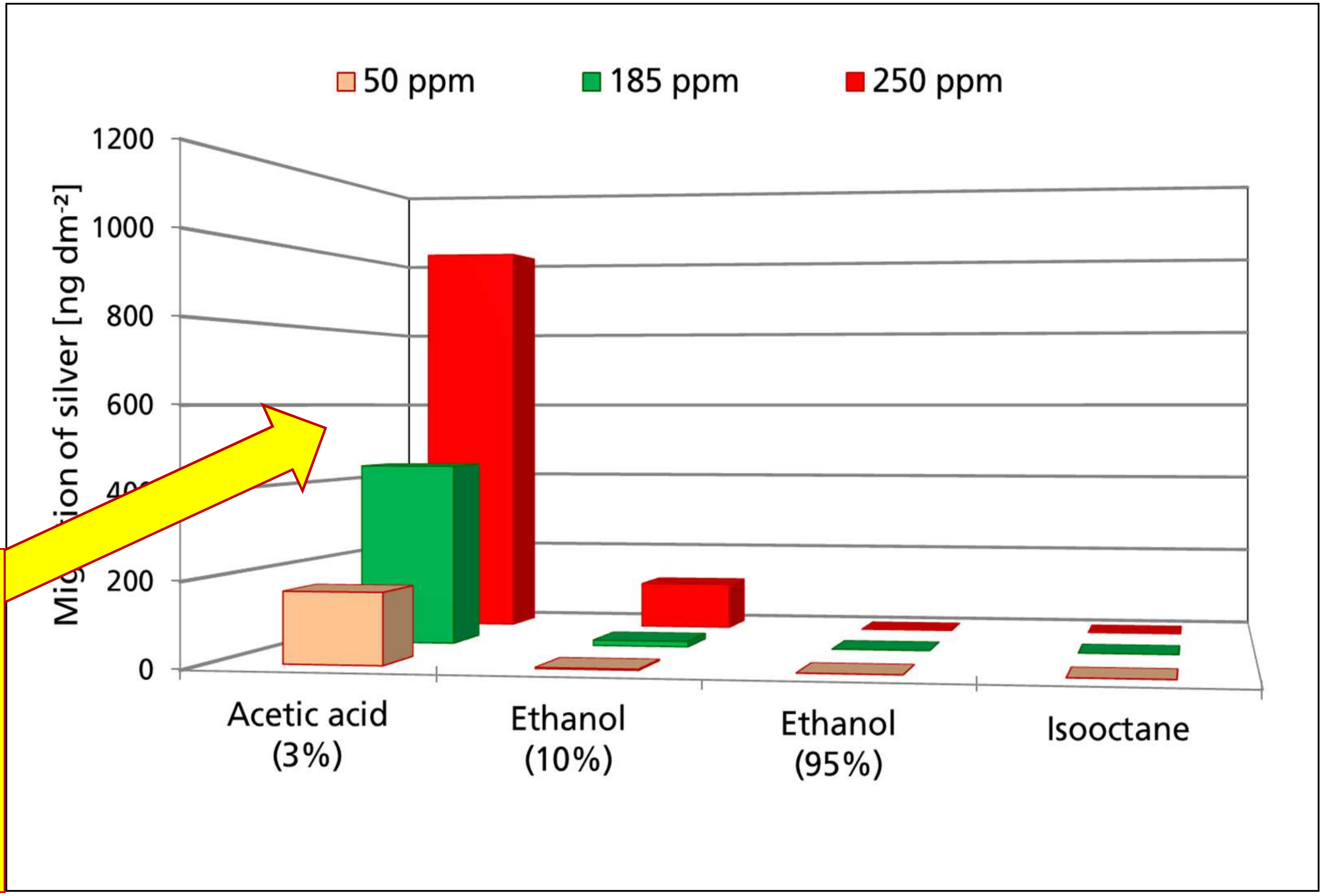
LDPE film (100 µm) with nano-silver at 250 ppm



Model system: nano silver in LDPE

Results:

Migration test
10 d @ 60°C
Ag determined by ICP-MS

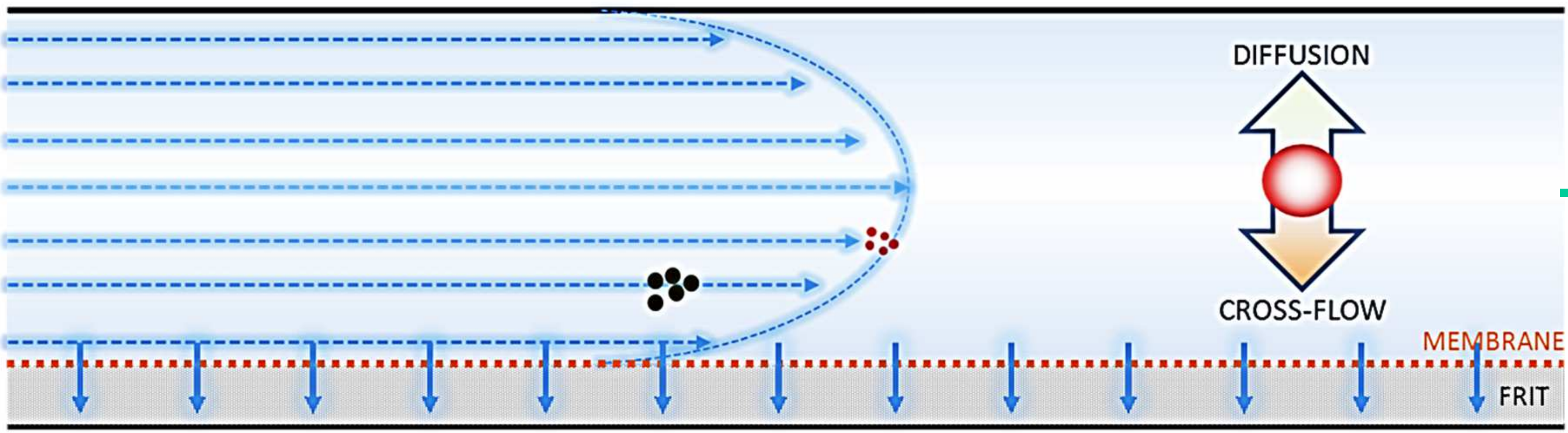


This is NOT nano silver but ionic silver (dissolved in 3% acetic acid)

AF4 analysis (Asymmetric Flow Field Flow Fractionation)

Sample injection

Detection via MALLS or ICP-MS

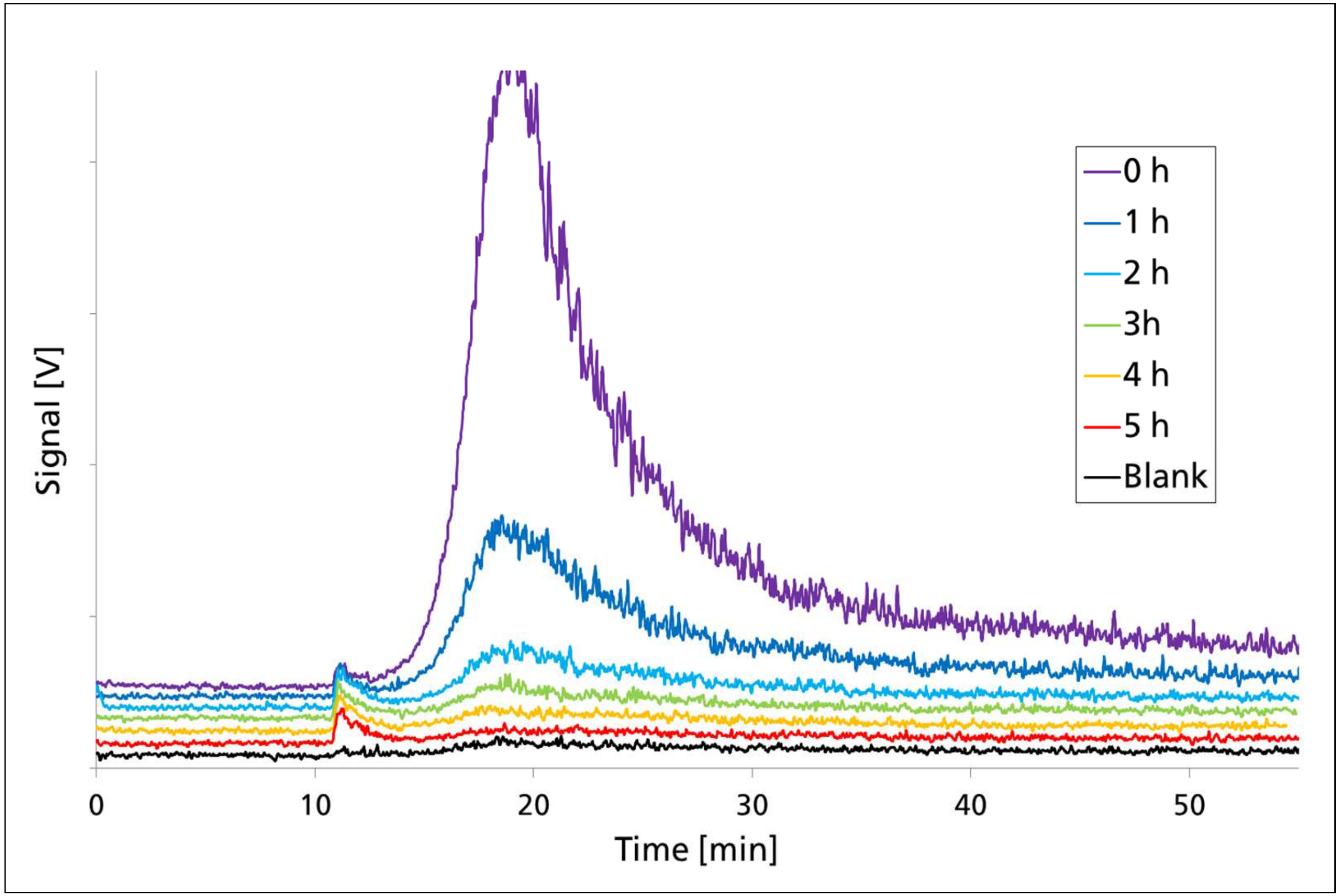


Separation based essentially on particle size

Model system: nano silver in LDPE

Results:

Stability test
3% acetic acid
5 h @ 23°C
Nano Ag
determined by
AF4 – MALLS



Nano Ag is oxidatively dissolved with a half life time $t_{1/2}$ = 0.6 h

Summary model system: nano silver in LDPE

Migration tests did not show detectable migration

of Ag nano-particles

at detection limits of ~ 0.1 to 0.5 ppb (µg/kg) food

independent of
- type of food simulant and
- nano additive concentration in polymer

Summary of all other test systems

In ALL cases, migration studies even when using exaggerated contact conditions of food simulants with the test films, no analytical (ICP-MS, AF4) observation of migrated nano-particles was obtained.

The achieved detection limits were dependent on the type of nano additive and ranged from 0.12 ppb - 0.5 ppb (µg/kg) food and were in two other cases at 5 ppb and 130 ppb.

Migration Modelling of NPs – why?

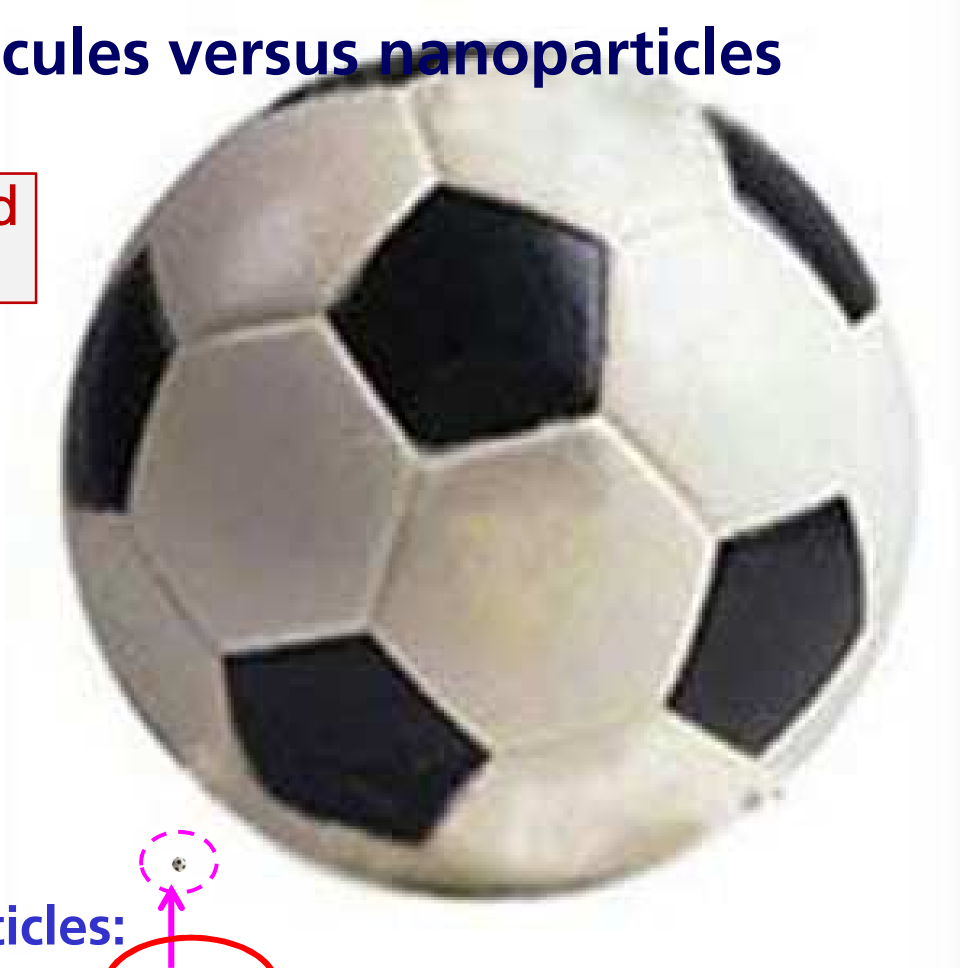
What does it mean
for nanoparticle migration,
when we measure
'not detected'
at levels of
0.1 ppb to 10 ppb?

A comparison of sizes: molecules versus nanoparticles

Molecular volumes and 'diameters' (assuming simplisticly spherical geometry) of some well-known molecules

Molecule (mol.weight g/mol)	Volume V (nm³)	'Diameter' d (nm)
Hydrogen H_2 (2)	0.010	0.27
Water (18)	0.019	0.33
Ethanol (46)	0.054	0.47
Benzophenone (182)	0.175	0.69
DEHP (390)	0.408	0.92
Irganox 1076 (530)	0.588	1.04
Irgafos 168 (647)	0.670	1.09
Irganox 1330 (775)	0.820	1.17
Irganox 1010 (1178)	1.190	1.31
Spherical particle with diameter of 1.31 nm	1.190	1.31

A comparison of sizes: molecules versus nanoparticles



Nano additives are large compared to usual plastics additives!

Moves very slowly or 'not at all' (not measurably) in polymers

Conventional additives
0.1 – 0.5 – 1 nm

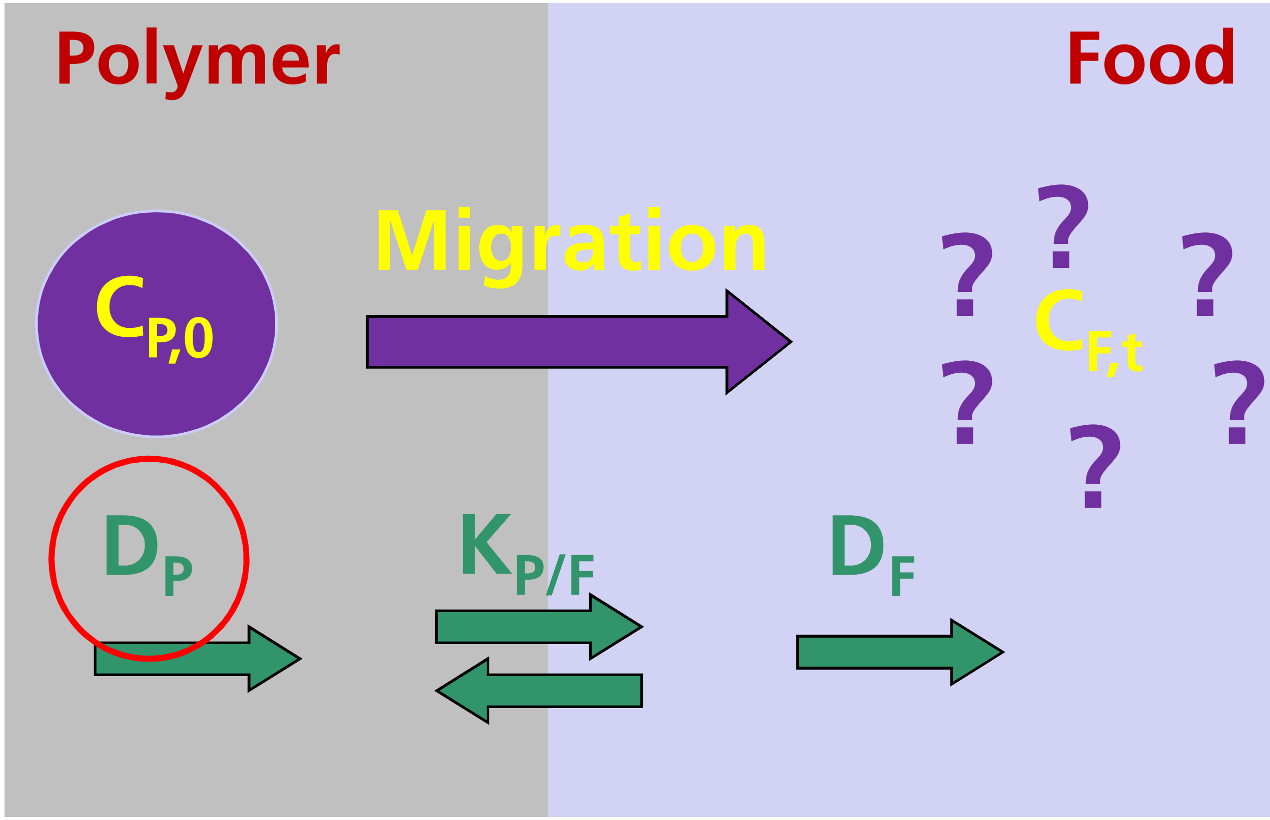
Nanoparticles:
20 nm - 1 nm - 100 nm

Migration modeling of nanoparticles

'Conventional' migration from FCM plastics can be modeled today …

…when mass transport follows Fickian Law

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2}$$



Key-Parameter: Diffusion & Partition coefficients D_P & $K_{P/F}$

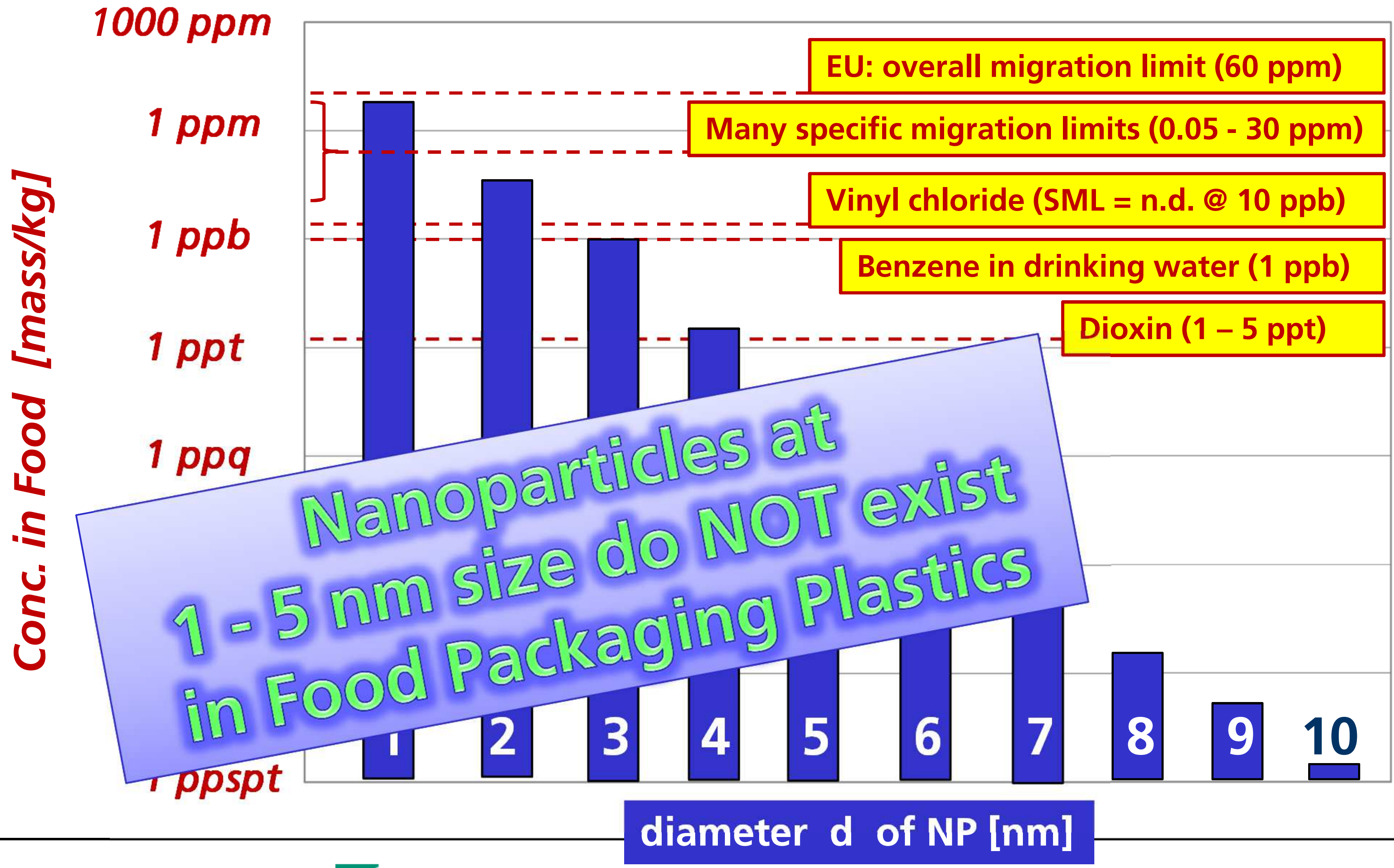
Migration modeling of nanoparticles – Diffusion coefficients

Diameter d_{NP} [nm]	Volume V_{NP} [nm³]	Diff' coeff. – LDPE D_P @ 40°C [cm²/s]	Diff' coeff. - PET D_P @ 40°C [cm²/s]
1.0	0.52	$3.0\ 10^{-9}$	$1.9\ 10^{-20}$
1.5	1.77	$1.9\ 10^{-11}$	$6.6\ 10^{-25}$
2.0	4.19	$1.4\ 10^{-13}$	$4.7\ 10^{-28}$
3.0	14.13	$3.9\ 10^{-17}$	$1.7\ 10^{-32}$
4.0	33.49	$5.4\ 10^{-20}$	$1.2\ 10^{-35}$
5.0	65.42	$2.1\ 10^{-22}$	$4.2\ 10^{-38}$
6.0	113.04	$1.7\ 10^{-24}$	$4.2\ 10^{-40}$
7.0	179.50	$2.4\ 10^{-26}$	$8.5\ 10^{-42}$
8.0	267.95	$4.8\ 10^{-28}$	$2.9\ 10^{-43}$
9.0	381.51	$1.3\ 10^{-29}$	$1.5\ 10^{-44}$
10.0	523.33	$4.4\ 10^{-31}$	$1.0\ 10^{-45}$

Franz R. & Welle F.: Mathematic modelling of migration of nanoparticles from food contact polymers; in: 'Nanomaterials/nanoparticles in Food Contact Materials: Design, Application, Safety.' (Ed. Rob Veraart) DEStech Publications ; in preparation.

Can nano particles migrate from FC plastics into foods?

Migration (10d@40°C) modeling of NPs (1000 ppm in LDPE)

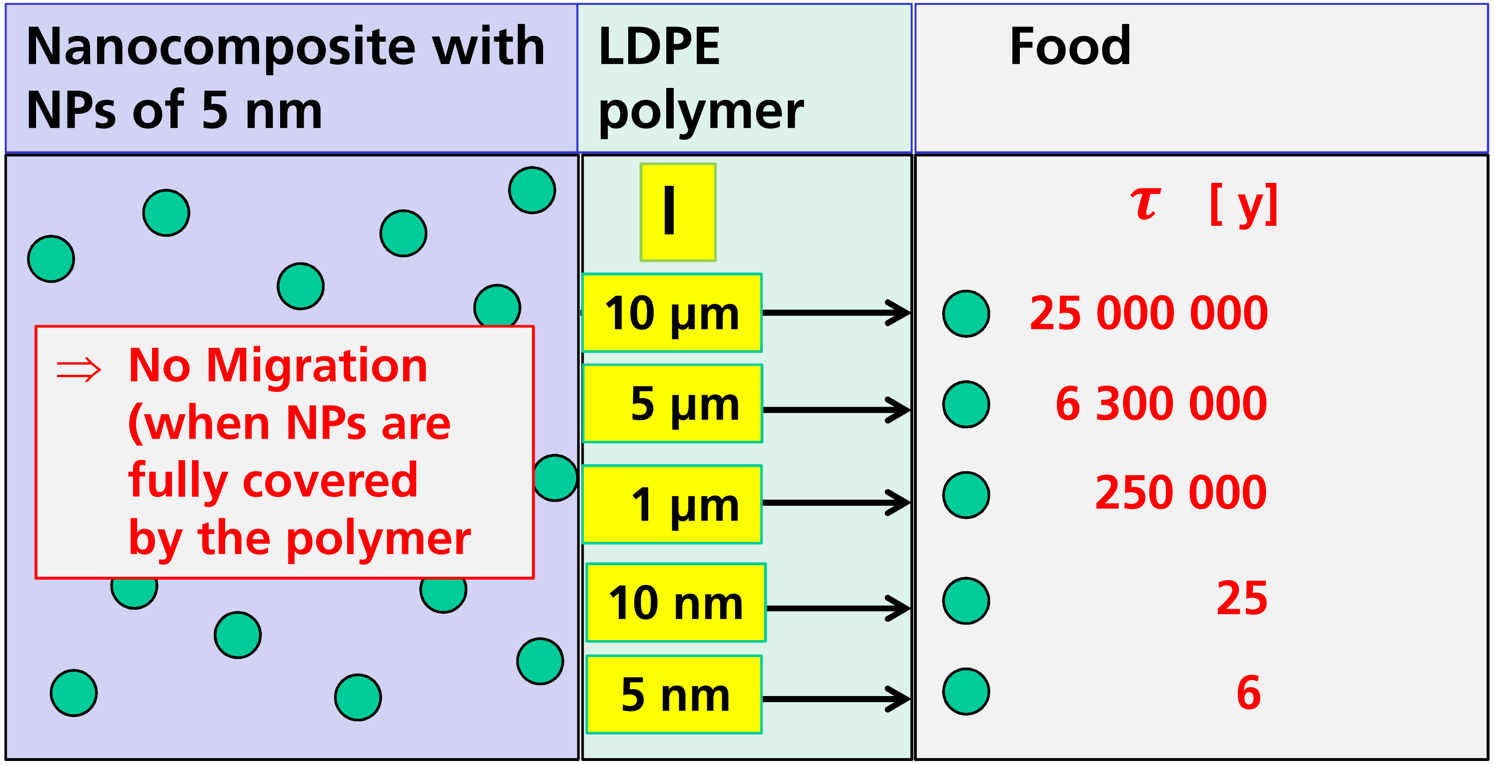


Fraunhofer
IVV

Migration modelling - lag times for NP (d = 5 nm) LDPE @ 40°C

5 nm (diameter) Nanoparticle @ 40°C => $D_{LDPE} = 2.1 \times 10^{-22}$ cm²/s

Lag time $\tau = l^2 / 6 D_P$



Conclusions

- Our migration studies did not show any evidence that NPs would migrate from host polymers such as LDPE, PS , PET into food simulants even under very severe test conditions.
- Migration modeling indicates that NP larger than 3 - 4 nm in diameter cannot migrate (following Fick'ian law of diffusion) at all from LDPE (and not from other FCM plastics).
- Our results underpin the assumption that NPs are immobilized when fully incorporated in FCM plastics (no direct contact). => exposure of the consumer via ingestion of packed food appears to be impossible and can be excluded.
- However, still to be explored more in depths: Can mechanical stress or strong interactions with foods (swelling) of the polymer surface cause physical release from FCM plastics? (Work is in hands ...)

Thank you!

We greatly acknowledge support of this work by

PlasticsEurope

Thanks also to

- 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)
- International Carbon Black Association ICBA
- Association of Synthetic Amorphous Silica Producers ASASP

Finally, thank you, Johannes Bott (our Ph.D. student), for the enormous amount of work invested into all these studies!