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Migration potential of nanomaterials in food contact plastics

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Agenda

- **Overview and summary of experimental model studies on the migration potential of ‚nano additives' from food contact plastics**
- **Migration modeling for nanoparticles from plastics – some calculations and visualisations of their migratability**
- **A view into an EFSA Opinion**
- **Conclusions**

Overview experimental model studies

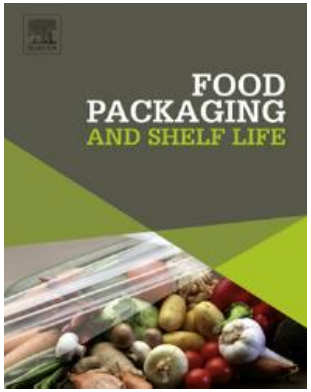
We did a series of experimental studies (migration tests and other) using LDPE polymer (high diffusion properties, worst case matrix) containing 'nano additives' at various concentrations:

- **Nano-sized titanium nitride, TiN**
  (listed in PIM – 20 ppm in PET)
- **Nano silver**
  (has been used in numerous studies)
- **Carbon black**
  (listed in PIM – 2.5% in polymer)
- **Synthetic amorphous silica (hydrophilic and silanated)**
  (listed in PIM – no restriction)
- **Laponite**
  (a very small nanoclay, still in hands, finished shortly)

Model system:

Nano titanium nitride (TiN) in LDPE

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.



Titanium nitride (TiN) in PET bottles for water and soft drinks – a very consumer relevant example

Technical function:

‘Reheat additive’ -
improves the thermal properties,
increase of production lots

Preforms for PET bottles

Model system: nano TiN in LDPE

Inhouse production of 3 different LDPE films (d = 60 µm) with TiN levels of …..

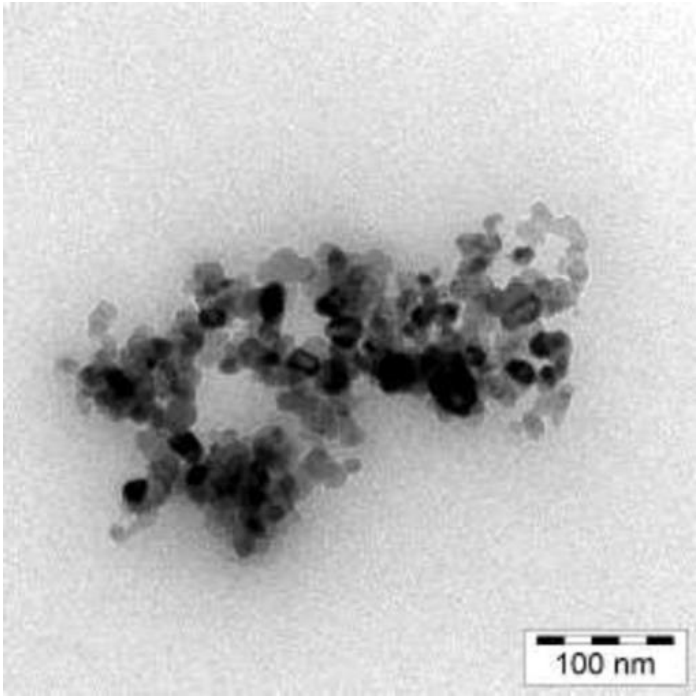
….0 ppm (blank), 100 ppm, 500 ppm, 1000 ppm

…using a masterbatch of nano TiN (20 nm) in LDPE

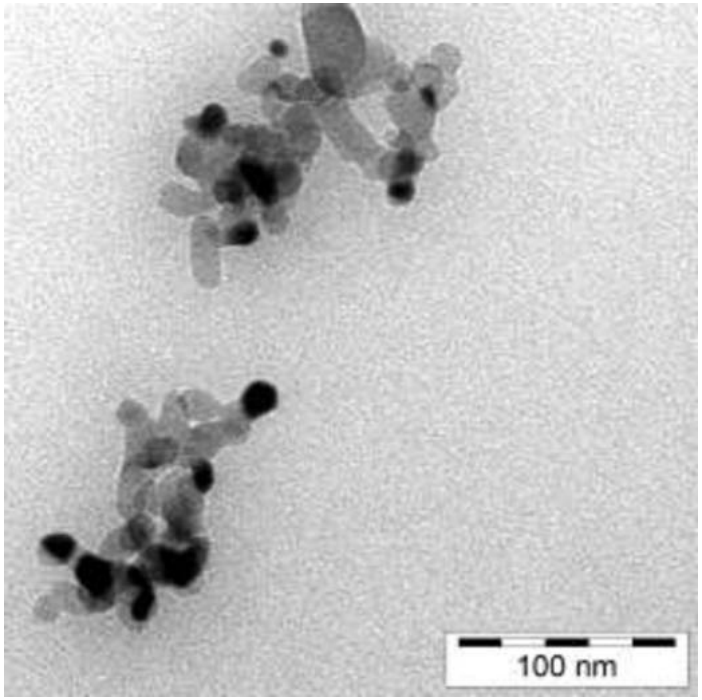
Model system: nano TiN in LDPE

TEM images of the LDPE film with nano TiN at levels of

100 ppm in LDPE



1000 ppm in LDPE



Migration potential of NPs in food contact plastics

Model system: nano TiN in LDPE

Results migration test **10 d @ 60°C** (Ti determined by ICP-MS)

Test film (LDPE)	Food simulant	Ti migration [µg/dm²]	Ti migration [µg/kg]
100, 500, 1000 ppm	3% acetic acid	n.d. ≤ 0.040	≤ 0.24
100, 500, 1000 ppm	iso-octane	n.d. ≤ 0.017	≤ 0.11
100, 500, 1000 ppm	95% ethanol	n.d. ≤ 0.018	≤ 0.11
100, 500, 1000 ppm	0.2 % Novachem	n.d. ≤ 0.016	≤ 0.09

Migration potential of NPs in food contact plastics

Model system:

Nano silver in LDPE

Bott J, Störmer A, and Franz R, 2014. 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, American Chemical Society, Washington DC, US. doi:10.1021/bk-2014-1159.ch005.

Migration potential of NPs in food contact plastics

Model system: nano silver in LDPE

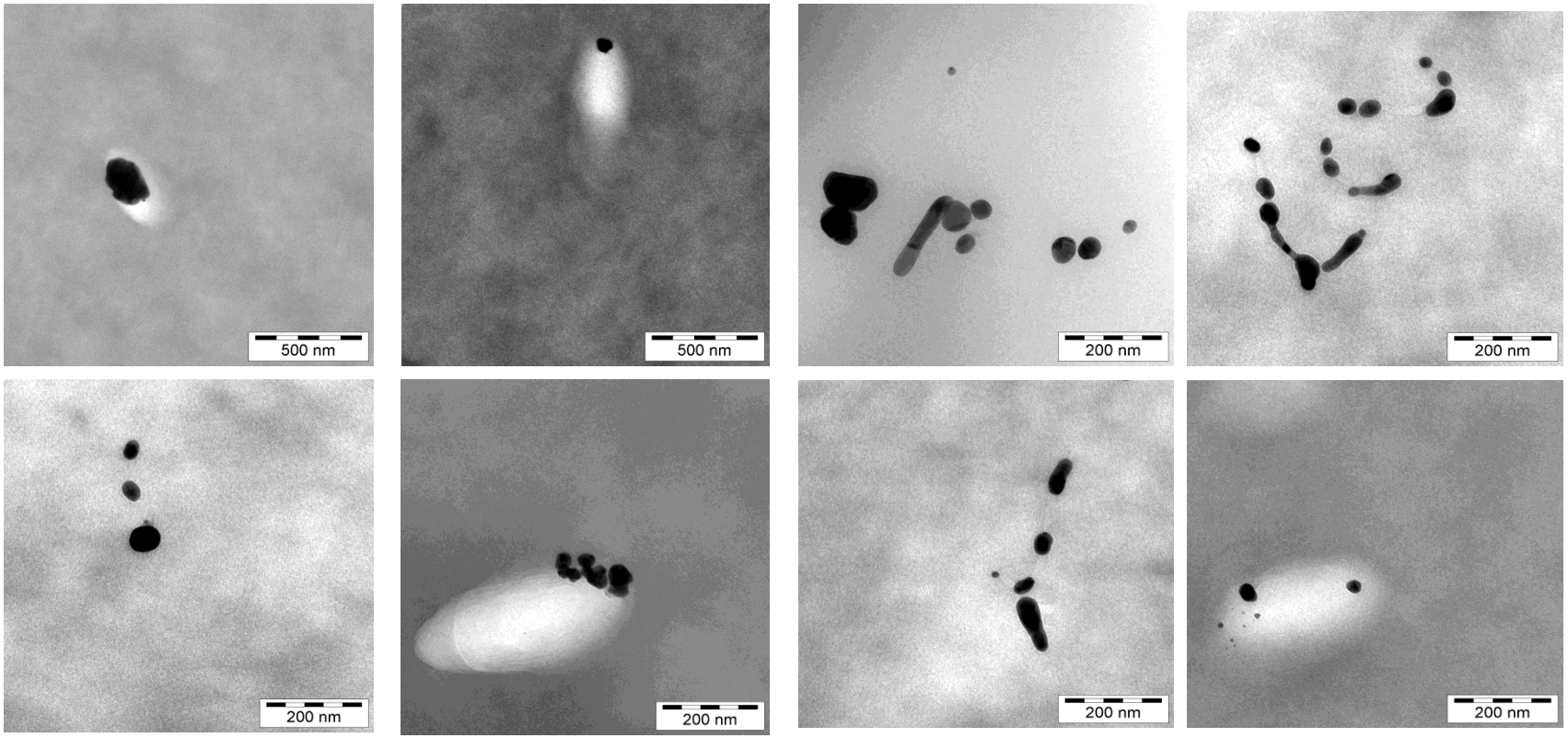
Inhouse production of 3 different LDPE films (100 µm) with nano silver at levels of …..

….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

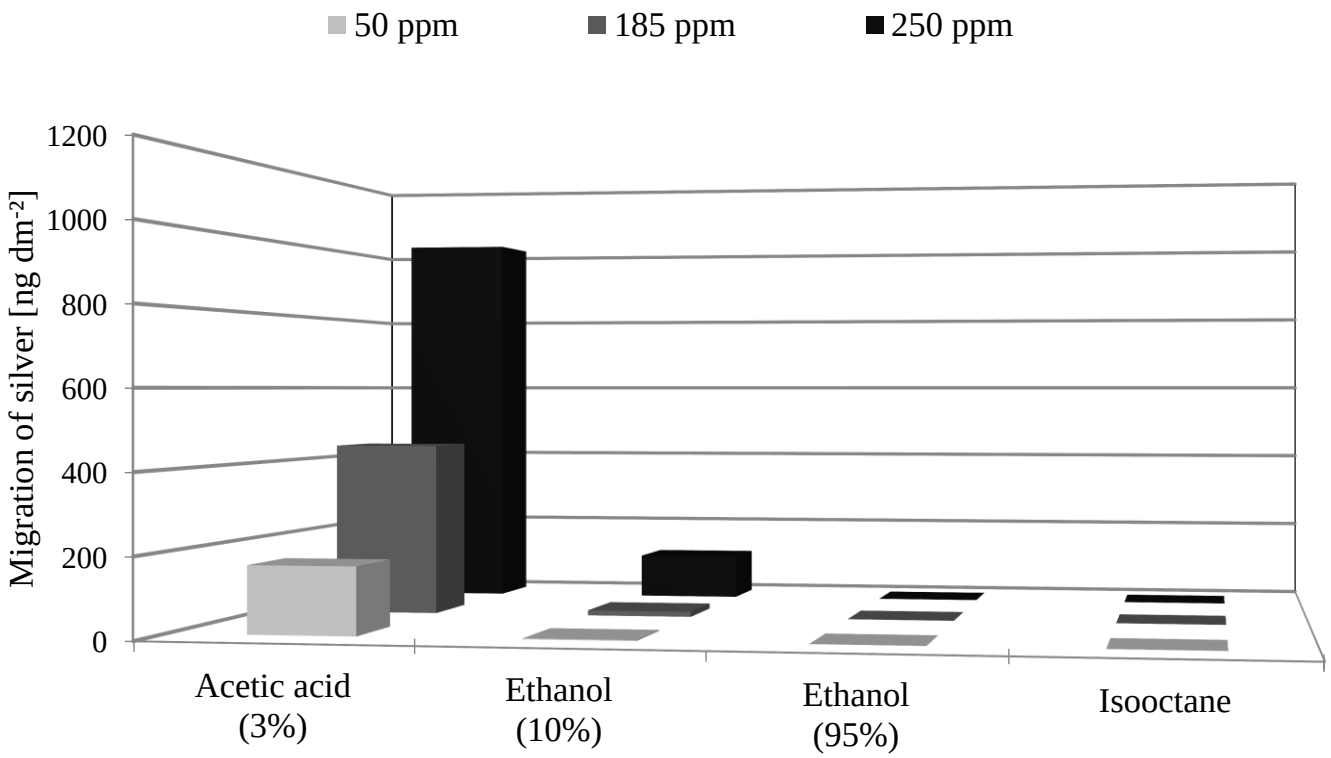


Migration potential of NPs in food contact plastics

Model system: nano silver in LDPE

Silver migration from nano Ag LDPE films after 10 days @ 60°C

Comparison:
3% acetic acid versus all other simulants (total silver measured by ICP-MS)

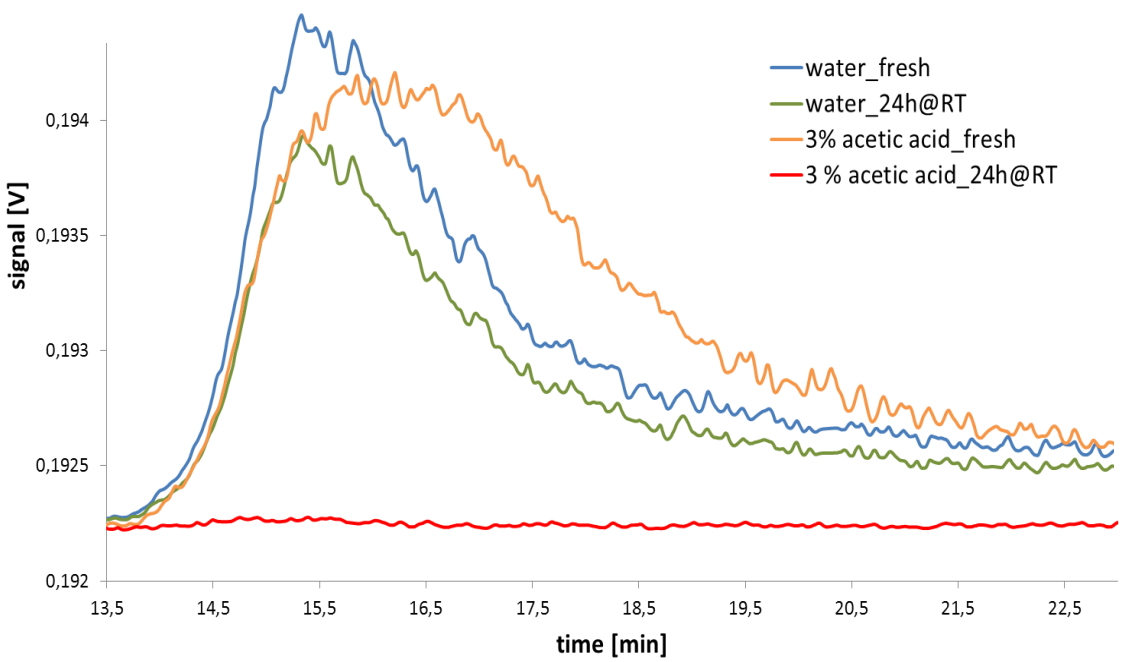


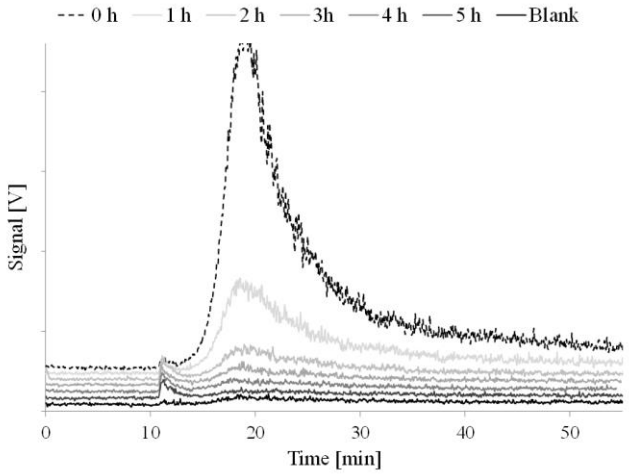
Migration potential of NPs in food contact plastics

Model system: nano silver in LDPE

Question: Is Ag as determined by ICP-MS nano Silver?

Test: AF4 analysis 1 ppm nano silver: silver rapidly dissolves to ions





Ag nanoparticles in 3 % acetic acid at RT:
Half life of particles: 0.6 h

Ag nanoparticles in 3 % acetic acid (orange, red) and water (blue, green) at RT.
In water 80 % of initial particles still present after 24 h.

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Model system:

Carbon Black in LDPE and PS

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.

Summary of all studies experimental results:

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 nanoparticles was obtained.

The achieved detection limits were dependent on the type of nano additive and ranged from 0.02 µg/dm² - 0.5 µg/dm² (0.12 µg/kg - 0.5 µg/kg food) and were in two other cases at 5 ppb and 130 ppb.

Migration modeling of nano particles from food contact plastics

Intention:

…. to support and substantiate our experimental results and other findings

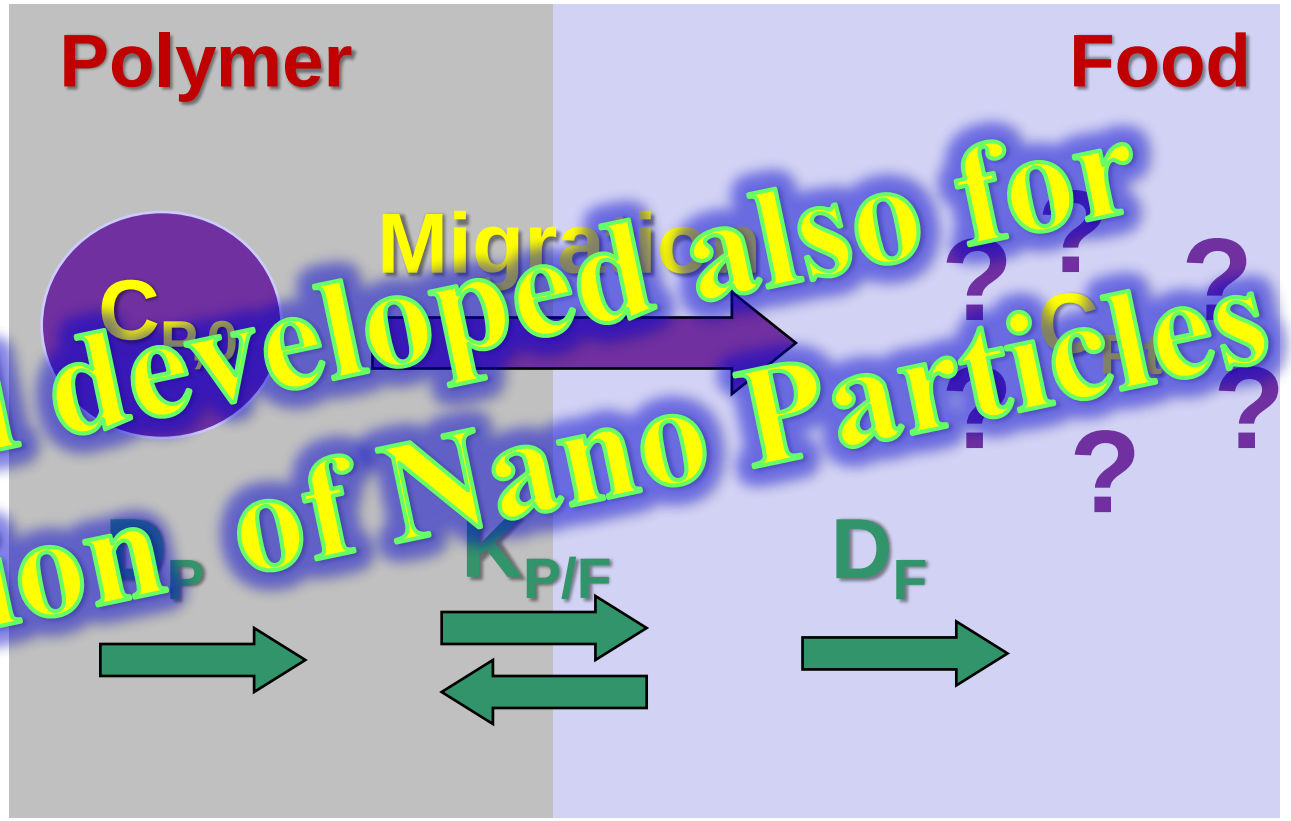
…. to explore into the concentration range not accessible to analytical determinations

Migration modeling of nanoparticles

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

…when mass transport follows Fickian Law

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



Model developed also for migration of Nano Particles

Key-Parameter: Diffusion coefficient D_P & partition constant $K_{P/F}$

Migration potential of NPs in food contact plastics

Migration modeling of NPs for PET

JOURNAL OF Applied Polymer SCIENCE

A New Method for the Prediction of Diffusion Coefficients in Poly(ethylene terephthalate)

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Correspondence to: F. Welle (E-mail: welle@ivv.fraunhofer.de)

$$D_P = b\left(\frac{V}{c}\right)^{a-\frac{1}{T}}{}^{d}$$

Parameter	Value
a	1.93 10^{-3} K^{-1}
b	2.37 10^{-6} cm^2 s^{-1}
c	11.1 $Å^3$
d	1.50 10^{-4} K^{-1}

Migration potential of NPs in food contact plastics

Migration modelling of nanoparticles - PET

$$D_P = f \text{ (molecular volume)}$$

Applied Polymer SCIENCE

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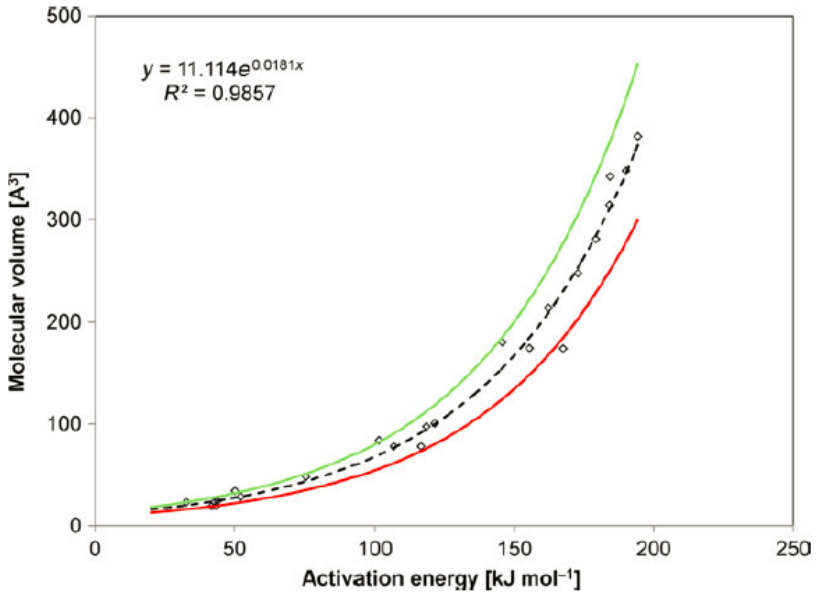

Figure 3. Correlation of the experimentally determined activation energy of diffusion E_A with the calculated volume of the migrants, red and green lines: variance of 20% on the molecular volume V. [Color figure can be

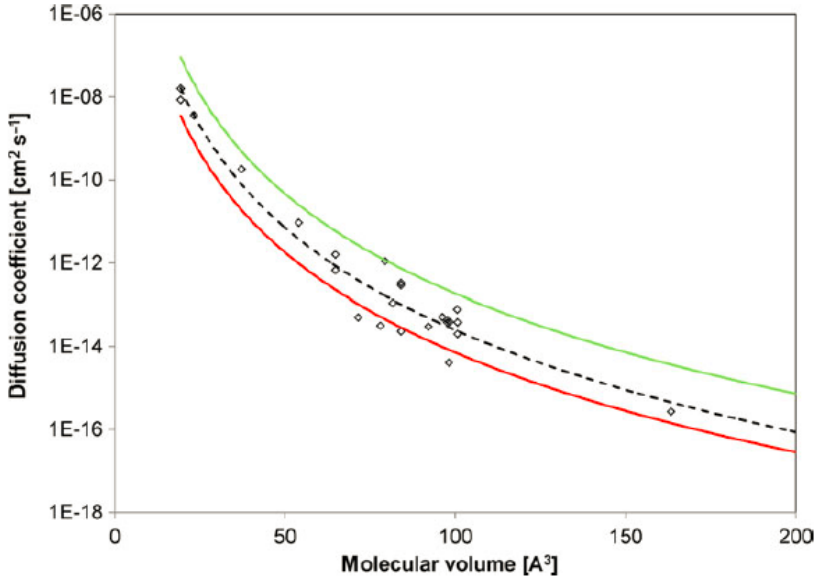

Figure 5. Correlation of literature of the diffusion coefficients in PET at 35°C and 40°C (Table 3 in Ref. 18) with the calculated molecular volume, black line: predicted diffusion coefficients from eq. (9), green and red line: variance of ±20% of the molecular volume V. [Color figure can be

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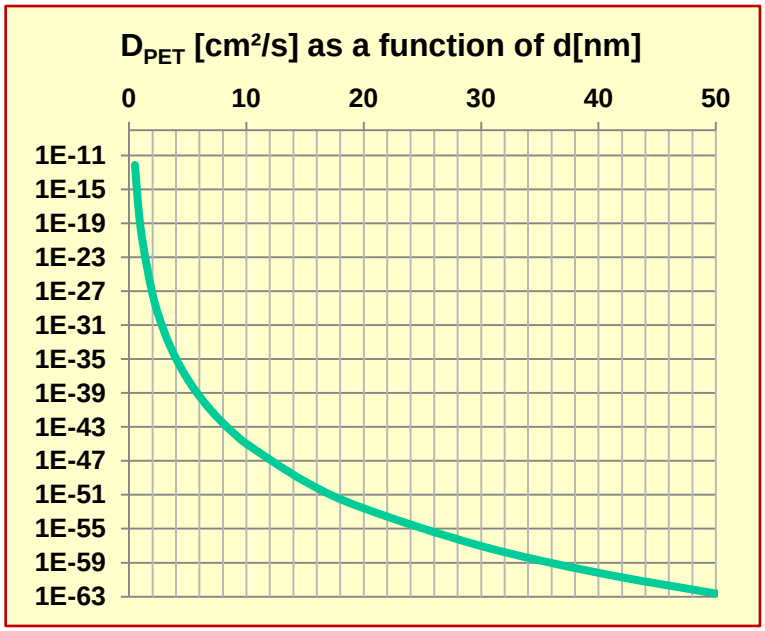
Migration potential of NPs in food contact plastics

Migration modeling for PET - diffusion coefficients at 40°C

Activation energy increases dramatically with d !
Diffusion coefficients become absurdly low!
=> No Migration



d [nm]	V [nm³]	E_a [kJ/mol]	D_{PET} [cm²/s]
0,5	0,1	98,3	7,726E-13
1	0,5	213,6	1,9026E-20
2	4,2	328,8	4,737E-28
3	14,1	396,3	1,6834E-32
4	33,5	444,1	1,1731E-35
5	65,4	481,2	4,1752E-38
6	113,1	511,5	4,1686E-40
7	179,6	537,1	8,4808E-42
8	268,1	559,4	2,905E-43
9	381,7	578,9	1,4814E-44
10	523,6	596,5	1,034E-45
15	1767,1	663,9	3,6743E-50
20	4188,8	711,7	2,5605E-53
30	14137,2	779,1	9,099E-58
40	33510,3	827,0	6,3408E-61
50	65449,8	864,1	2,2568E-63

Migration potential of NPs in food contact plastics

Model study & migration modeling of nanoparticles

Recently published

FOOD PACKAGING AND SHELF LIFE 2 (2014) 73–80

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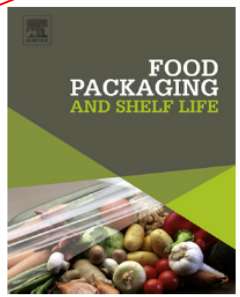

A model study into the migration potential of nanoparticles from plastics nanocomposites for food contact

CrossMark

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Migration modelling of nanoparticles - Polyolefines

For PO's a correlation between molecular volume and activation energy respectively diffusion coefficient as established for PET is not available.

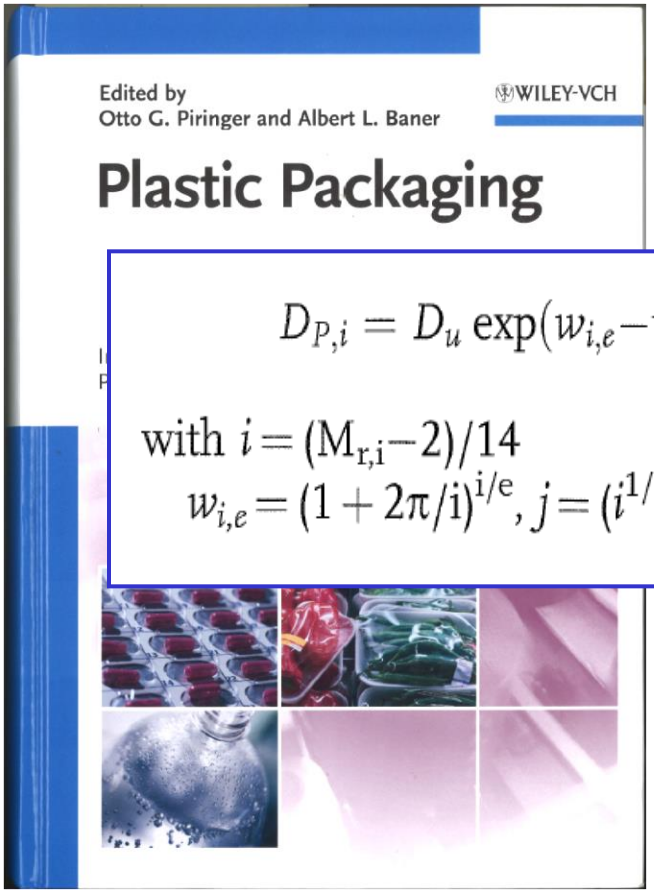
⇒ Need of a different approach

IDEA:

- Surrogate Nanoparticles with worst case character: spheres consisting or a material with low molecular weight (m.w.) and assuming a low density
- Calculate m.w. as a function of diameter
- Calculate D_P as function of m.w. using the PIRINGER's equation (socalled 'exact equation')

Migration potential of NPs in food contact plastics

Migration modelling of nanoparticles - polyolefines



$$D_{P,i} = D_u \exp(w_{i,e} - w_{p,e} \cdot 0.14(14j+2)^{2/3} - ww_{j,e}^{2/3} T_{m,p} R/RT) \qquad (6.28)$$

with $i = (M_{r,i} - 2)/14$

$w_{i,e} = (1 + 2\pi/i)^{i/e}$, $j = (i^{1/3})$, $w_{j,e} = (1 + 2\pi/j)^{j/e}$, $p = (M_{r,p}/14)^{1/3}$, $w_{p,e} = (1 + 2\pi/p)^{p/e}$

PIRINGER equation (6.28): so-called ‚exact' equation for Polyethylene < T_{mp}

$D_{P,i}$ = f (T, m.w.$_{Migrant}$, m.w.$_{Polymer}$, T(m.p.)$_{Polymer}$

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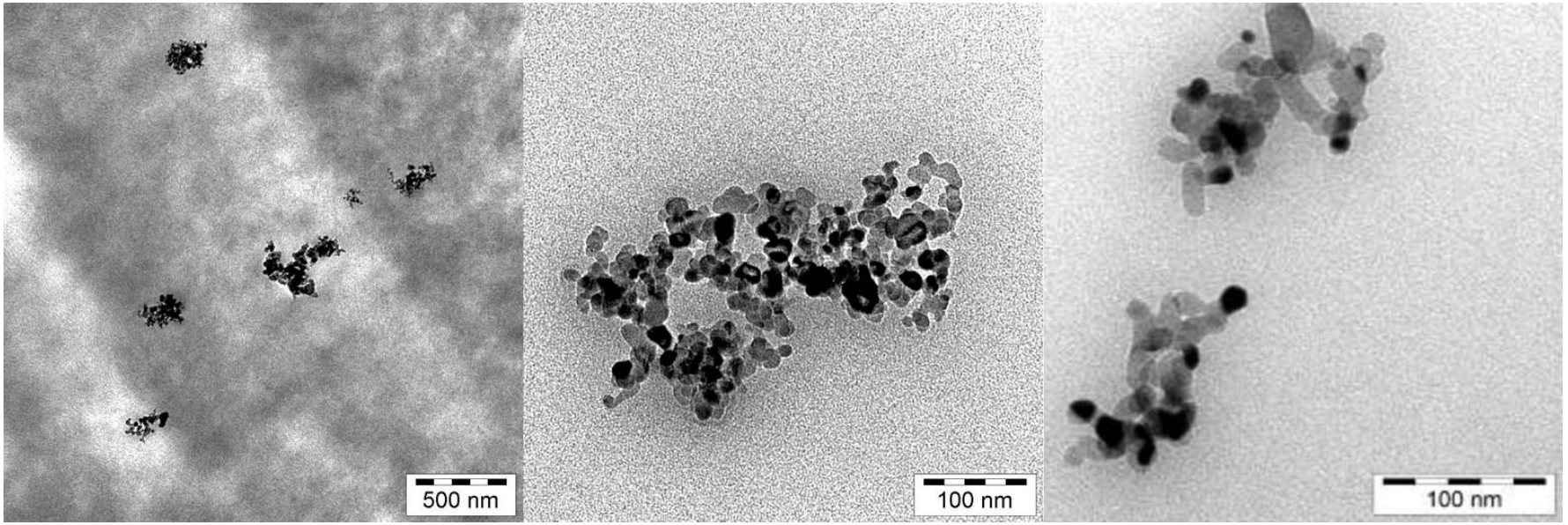
Migration potential of NPs in food contact plastics

Migration modeling of nano particles:

Example: 1000 ppm of NP (TiN) in LDPE (d = 3 mm)

Contact: 10 days @ 40°C



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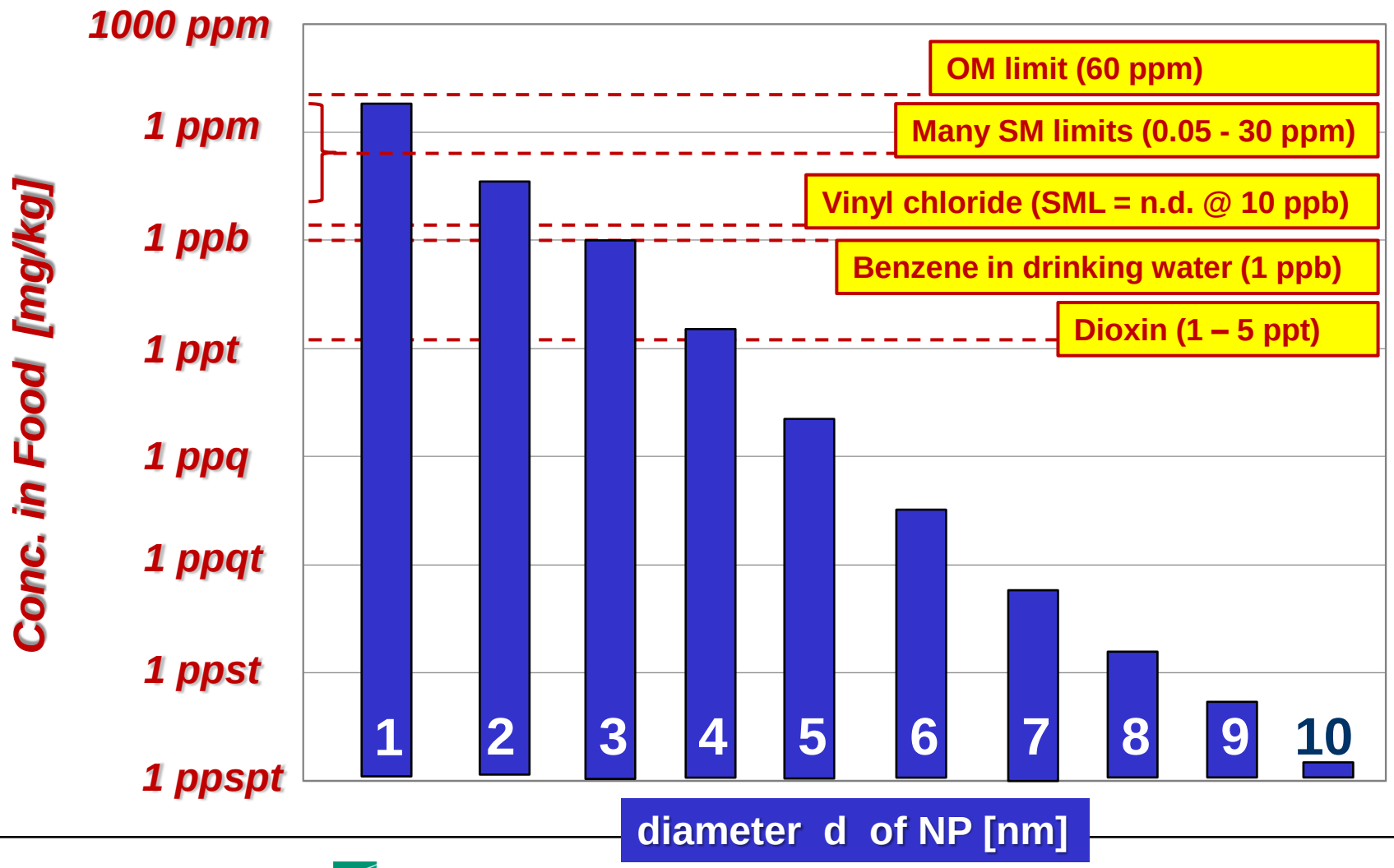
Can nano particles migrate from FC plastics into foods?

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



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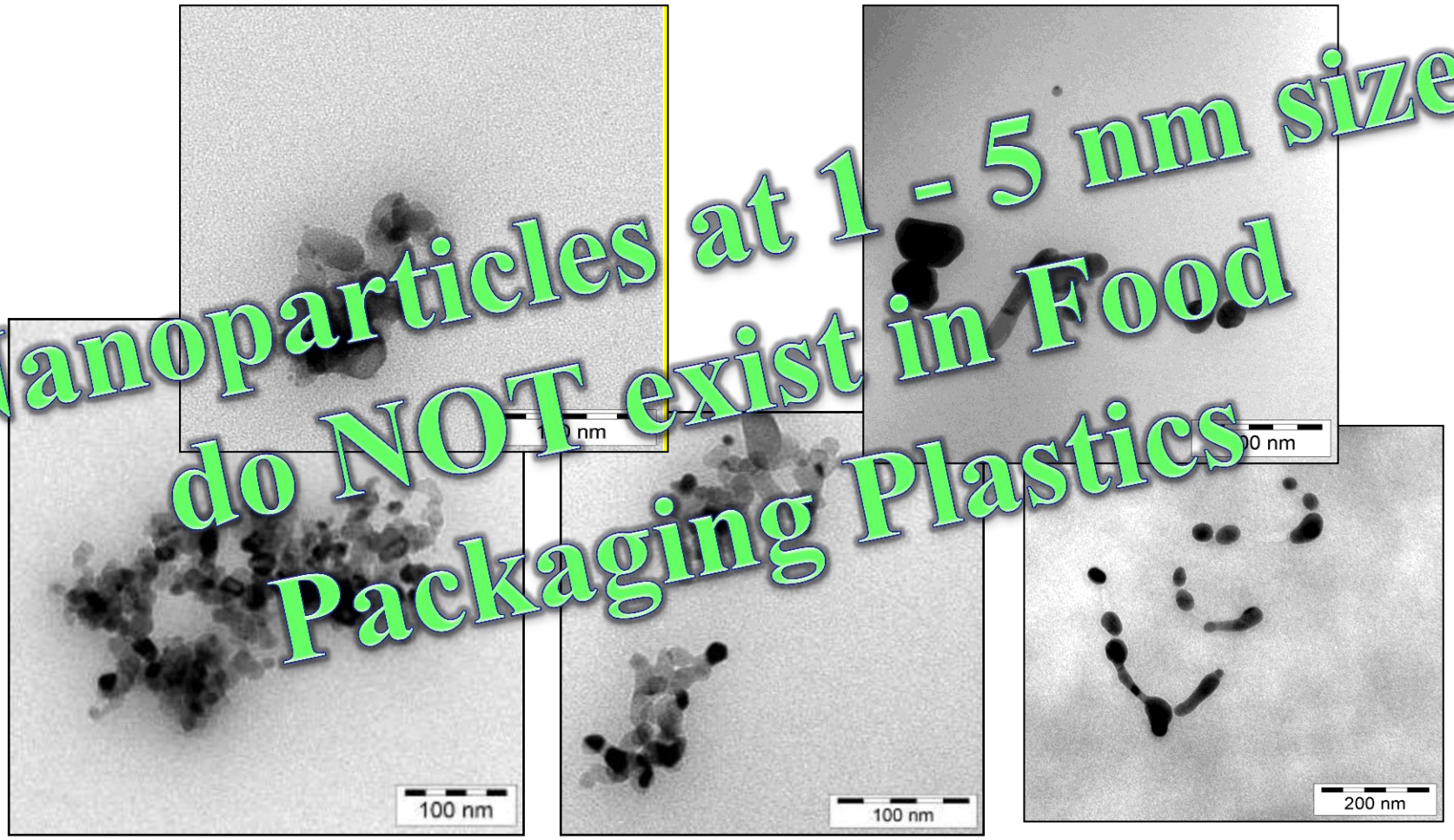
Can nano particles migrate from FC plastics into foods?



Nanoparticles at 1 - 5 nm size do NOT exist in Food Packaging Plastics

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Migration potential of NPs in food contact plastics

EFSA opinion on an additive (impact modifier in PVC) in nanoform

European Food Safety Authority

EFSA Journal 2014;12(4):3635

SCIENTIFIC OPINION

Scientific Opinion on the safety assessment of the substances (butadiene, ethyl acrylate, methyl methacrylate, styrene) copolymer either not crosslinked or crosslinked with divinylbenzene or 1,3-butanediol dimethacrylate, in nanoform, for use in food contact materials[1]

EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids (CEF)[2, 3]

European Food Safety Authority (EFSA), Parma, Italy

Migration potential of NPs in food contact plastics

EFSA opinion on an additive (impact modifier in PVC) in nanoform

"Recognized migration modelling, as currently settled, is not directly applicable to nanoparticle migration estimation. For this reason, the applicant applied additional conservative assumptions to estimate migration of the nanoparticles from the nanocomposite material, in particular the assumption that all particles had a size less than 10 nm. The estimated migration was 1 $x10^{-6}$ mg/kg food. **Real migration, if any, is expected to be even lower and therefore consumer exposure would be very low, if any** (Bott et al., 2014).
Consequently, **the Panel considered that the intended use of these nanoparticulate substances does not give rise to exposure of the consumer via food** and therefore would not be of toxicological concern if used only in rigid PVC individually or in combination up to a total of 10 % w/w and for the food contact applications described."

Bott J, Störmer A, and Franz R, 2014. 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, American Chemical Society, Washington DC, US. doi:10.1021/bk-2014-1159.ch005.

Conclusions

- Our migration studies did not show any evidence that NPs would migrate from the LDPE host polymer 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 therefore not from any plastics FCM. For PET, the cut-off value would be below 1 nm. However, usual primary NPs are already larger. And, due to aggregation and agglomeration of NP such small single NP do not occur in FCM.

Conclusions

- Experimental results and theoretical considerations (migration modeling) strongly underpin the assumption that NPs are immobilised when fully incorporated in FCM plastics (no direct contact).

  From this exposure of the consumer via ingestion can be excluded.

- Whether mechanical stress or strong interactions with foods (swelling) of the polymer surface may cause physical release should be considered in the particular case and be checked.

Thank you!

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- PlasticsEurope
- 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

which is greatly acknowledged!

Many thanks also to Johannes Bott, our Ph.D. student who has done the experimental work including test sample preparations.