Nanoparticles in Organic Solvents with Polymers
Stability and Consequences Upon Material Synthesis Through Spray Drying

Martin Rudolph, Urs A. Peuker
Outline

1) Motivation
2) Solution Method
3) Preliminary Investigations
4) Theory of Nanoparticle Interactions
5) Experiments - Stability
   a) Destabilization with non-adsorbing PMMA, PC, PS
   b) Stabilization with adsorbing PVB
6) Summary and Conclusion
• Synthesis of highly filled polymer nanoparticle composites ($\phi_{\text{Nano}} > 10\%$)

Magnetic Beads for sorptive Bioseparation

Hickstein, B., Peuker, U.A.
J Appl Poly Sci, 112, 2366
1 Motivation

- Synthesis of highly filled polymer nanoparticle composites ($\phi_{\text{Nano}} > 10\%$)

Composite Micropowder for Micro Injection Molding
1 Motivation

- Synthesis of highly filled polymer nanoparticle composites ($\varphi_{\text{Nano}} > 10\%$)
- Overcoming problem of dispersing (deagglomeration + mixing)
1 Motivation

• Synthesis of highly filled polymer nanoparticle composites ($\varphi_{\text{Nano}} > 10\%$)

• Overcoming problem of dispersing (deagglomeration + mixing)

• We present an alternative modular process with the solution and spray drying method
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2 Solution Method

- **Polymers**
  - Poly(methyl methacrylate)
  - Poly(vinyl butyral)
  - Poly(bisphenol A carbonate)

- **Nanoparticles**
  - Fe₃O₄ magnetite, superparamagnetic

- **Solvent(s)**
  - Dichloromethane
  - Ethyl Acetate

- **Surfactants**
  - Carboxylic acids (C14 - C18)
2 Solution Method

Fe₂O₄ - Precipitation

Liquid-Liquid-Phasetransfer

Adding solved Polymer

Spray Drying of Organosol

x_{\text{Crystallite}} \approx 15 \text{ nm}

H₂O

organic solvent

Surfactant

Polymer coil

Pressagglomeration

Micro injection molding

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Investigations with TEM and pc-AFM

• TEM
good distribution for spray dried microcomposite particle

TEM, spray dried particle

PMMA49  RS21  MAG30
3 Preliminary Investigations

Investigations with TEM and pc-AFM

- TEM
  good distribution for spray dried microcomposite particle

- phase contrast AFM
  shows good distribution in an injection moulded sample

  Rudolph, M. *Chem Ing Tech*, 82, 2189 (2010)

- **BUT**: both investigations only have a very narrow field of view

  phase contrast AFM, injection moulded sample

PMMA64  RS06  MAG30

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Investigations with TEM and pc-AFM

- phase contrast AFM
  large areas of higher phase values

phase contrast AFM, injection moulded sample

PMMA64  RS06  MAG30

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3 Preliminary Investigations

Investigations broad field pc-AFM and BSE-SEM

- phase contrast AFM
  large areas of higher phase values

- similar „clusters“ for BSE-SEM

back scattering electron SEM, sample as before

PMMA64  RS06  MAG30
3 Preliminary Investigations

Agglomerates? / Primary Particles?

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3 Preliminary Investigations

Investigations broad field pc-AFM and BSE-SEM

PMMA61 – RS09 – MAG30  PMMA40 – RS10 – MAG50

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3 Preliminary Investigations

Where are they from?

PMMA61 – RS09 – MAG30

PMMA40 – RS10 – MAG50

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3 Preliminary Investigations

Fe$_2$O$_4$ - Precipitation

Liquid-Liquid-Phasetransfer

Adding solved Polymer

Spray Drying of Organosol

X$_{\text{Crystallite}} \approx 15$ nm

H$_2$O

organic solvent

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• strong VAN DER WAALS attraction leads to agglomeration

• stabilization against agglomeration with surfactants by liquid-liquid phase-transfer

Machunsky, S. *Coll & Surf A*, 348, 186 (2009)

surfactant of choice: ricinoleic acid


surfactant of choice: ricinoleic acid

• strong VAN DER WAALS attraction leads to agglomeration

• stabilization against agglomeration with surfactants by liquid-liquid phase-transfer
4 Theory of Nanoparticle Interactions

\[ h = \frac{H}{r} \]

\[ E_{\text{vdW Attraction}} = -\frac{C_H}{6} \left[ \frac{2}{h^2 + 4h} + \frac{2}{(h+2)^2} + \ln \left( \frac{h^2 + 4h}{(h+2)^2} \right) \right] \]

\[ E_{\text{entrop Repulsion}} = \begin{cases} 
2 \cdot \pi \cdot r^2 \cdot \frac{\Phi}{A_{\text{FattyAcid}}} \cdot k \cdot T \cdot \left( 2 - \frac{(h+2) \cdot r}{\delta} \cdot \ln \left( \frac{1+\delta/r}{1+h/2} \right) - \frac{h \cdot r}{\delta} \right) , & \frac{h \cdot r}{2 \cdot \delta} < 1 \\
0 , & \frac{h \cdot r}{2 \cdot \delta} > 1 
\end{cases} \]

\[ E_{\text{interaction}} = E_{\text{vdW Attraction}} + E_{\text{entrop Repulsion}} + E_{\text{Born}} \]

Rosensweig, R.E. *A.I.Ch.E.Symp.Ser.*, 5, 104 (1965)
4 Theory of Nanoparticle Interactions

\[ \Phi = 50\% \]

\[ \delta = 2.2 \text{ nm} \]

The thickness of the adsorption layer \( \delta \) is shown for different values of \( E_{\text{interaction}} \) in kT. The graph illustrates the interaction energy \( E_{\text{interaction}} \) as a function of the thickness \( \delta \) and the distance \( H \) in nm.

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4 Theory of Nanoparticle Interactions

\[ \Phi = 50\% \]

Thickness of adsorption layer \( \delta \)

\[ \delta = 2.2 \text{ nm} \]

\[ \delta = 0 \text{ nm} \]

\[ E_{\text{interaction}} \text{ in } kT \]

\[ H \text{ in nm} \]

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4 Theory of Nanoparticle Interactions

\[ \delta = 2.2 \text{ nm} \]

Surface coverage fraction \( \Phi \)

\[ E_{\text{interaction}} \text{ in } kT \]

H in nm

\( \Phi = 0 \)

\( \Phi = 1 \)
• strong \textit{VAN DER WAALS} attraction leads to agglomeration

• stabilization against agglomeration with surfactants by liquid-liquid phase-transfer

• stability effects by \textit{polymer} addition
Depletion interaction – Phase diagrams


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5 Experiments – stability

• assessment of the mass concentration of primary particles \( w_{\text{primary}} \)

• centrifugation and determination of the concentration with TGA, Photospectrometer

\[ \text{increasing } c_{\text{Poly}} \]

diluted supernatant after centrifugation,

\( x_{\text{primary, supernatant}} < 40 \text{ nm} \)


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5a Destabilization with non-adsorbing polymers

Destabilization: decreasing primary particle concentration with increasing polymer concentration

$c_{\text{Mag}} = 24.4$ g/l

F in %

$W_{\text{Primary in } \%}$

$c_{\text{Poly in g/l}}$

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kinetics of coagulation: not rapid → fast drying after mixing should reduce large amount of agglomerates

$k_{Mag} = 1.2 \text{g/l}$

$c_{Poly} = 58.9 \text{ g/l}$
5a Destabilization with non-adsorbing polymers

kinetics of coagulation: problem of comparability to stability investigation due to very low colloid concentration

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\[ c_{\text{Mag}} = 1.2 \text{g/l} \]
\[ c_{\text{Poly}} = 58.9 \text{ g/l} \]
5a Destabilization with non-adsorbing polymers

- Nano-Fe$_3$O$_4$ dispersion under microscope with $c_{\text{Mag}} = 1.5$ g/l
- addition of PMMA leads to larger light-optically visible agglomerates, $\tau = 15$ min
• Nano-Fe$_3$O$_4$ dispersion under microscope with $c_{\text{Mag}} = 1.5$ g/l

• addition of PMMA leads to larger light-optically visible agglomerates

• inverted BSE-SEM of spray dried particles PMMA64-RS06-MAG30 show agglomerates as well
Destabilization with non-adsorbing polymers

- similar agglomerate sizes for dispersion and moulded BSE-SEM crosssection
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5b  Stabilization with adsorbing polymer

stabilization: increasing primary particle concentration with increasing polymer concentration

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5b  Stabilization with adsorbing polymer

particle size: increase in particle size with adsorbing polymer layer forming, of Langmuir type (line)

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adsorption isotherm: Langmuir type
adsorption of PVB on sterically stabilized nanomagnetite

\[ \Gamma = \Gamma_{\text{max,PVB}} \cdot \frac{k \cdot c_{\text{Poly}}}{1 + k \cdot c_{\text{Poly}}} \]

\[ \Gamma_{\text{max,PVB}} = 0.497 \text{ g/g} \]

\[ k = 0.04 \]

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Solution and spray drying process is suitable for nanocomposite synthesis.

HOWEVER: nanoparticle interactions have to be considered.

Added, solved polymers will influence nanoparticle interaction.

Stabilization through adsorbing polymers reveals suitability of the solution method.
Thanks for your interest!

Meet me at poster D-PO3-20
» Nanofix – Nanoparticle-wax-formulations as Additives for Extruder Compounding«
Filler Homogeneity – SEM Analysis ($F = 30\%$)

**B-SEM cross section** → **Binary** → **Voronoï** → **Coefficient of variance - cov**

- **Compounding**
  - $\text{cov}(A) = 5.45$

- **Solution/Drying**
  - $\text{cov}(A) = 0.98$

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Phase contrast AFM analysis

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PMMA49 – RS21 – MAG30

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Phase contrast AFM analysis

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• Composition

\[ D \text{ – surfactant (detergent) ratio} \]

\[ D = \frac{m_{\text{surfactant}}}{m_{\text{nano}}} \]

\[ n_{\text{nano}} \cdot (\text{surfactant} + m_{\text{polymer}}) \]

\[ \text{polymer concentration} \]

\[ \phi_{\text{Poly}} \]

\[ x \text{ in nm} \]

\[ 0.00 \quad 0.05 \quad 0.10 \quad 0.15 \quad 0.20 \quad 0.25 \]

\[ D \text{ in g/g} \]

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Supplemental

- Interparticle Distance

\[ ID = x \cdot \left[ \left( \frac{\pi}{3 \cdot \varphi_{nano}} \right)^3 \cdot \sqrt{3/4} - 1 \right] \]

\[ \varphi_{nano} = \frac{\rho_{polymer}}{\rho_{nano}} \left[ \frac{1}{F} + D \left( \frac{\rho_{polymer}}{\rho_{surfactant}} - 1 \right) - 1 \right]^{-1} \]
$c_{\text{Poly}} = \frac{\rho_{\text{DCM}} \cdot \left[ c_{\text{solid}} - c_{\text{solid}} \cdot F \cdot (1 + D) \right]}{1 - c_{\text{solid}}}$
Supplemental

- Gravimetric Characterisation with TGA/FTIR

-- characteristic mass-loss

\[
\chi_{\text{Stokes}} = (20 \pm 2) \text{ nm}
\]

\[
W_{\text{Mag,overall}}
\]

\[
W_{\text{Mag,centri}}
\]
Supplemental

- Segregation Effects with Spray Drying

<table>
<thead>
<tr>
<th>fraction</th>
<th>$x_{50,3}$</th>
<th>$w_{Mag}$</th>
<th>$\Delta m(600^\circ C-800^\circ C)$ / $w_{Mag}$</th>
<th>yield</th>
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<tbody>
<tr>
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TGA

PSD

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Supplemental

- Spray Drying
- Büchi lab scale spray dryer co-current, inert-loop
- $x_{50, \text{composite}} \approx 4 \, \mu m$
- up to 100g/h composites

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