Size and Shape Characterization of Prolate Particles

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ICT PRAGUE

CPPS-Lecture
ad Units 9 and 14

EBERHARD KARLS UNIVERSITÄT TÜBINGEN

Introduction 1

- **Size** and **shape** characterization of strongly **anisometric particles** and **particle systems** (platelet and fiber systems) poses severe theoretical and practical problems.
- **Flaky particles (platelets):** Shape information can be extracted from a comparison of sedimentation and laser diffraction data *(PABST et al. 2000, 2001, 2002):*

$$\Psi = \frac{3\pi}{4}\left(\frac{D_L}{D_S}\right)^2$$

D_L = laser diffraction equivalent diameter (closely related to the true disc diameter), D_S = sedimentation equivalent diameter (Stokes diameter), Ψ = "LS shape factor" (closely related to the aspect ratio).

Introduction 2

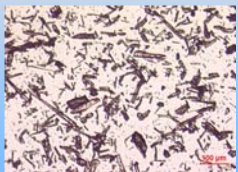
- **Elongated particles (fibers):** Fiber orientation effects in the flow cell of laser diffractometers (alignment in the flow direction) can lead to strongly non-circular diffraction patterns and can have a strong impact on the results *(BERTHOLD et al. 2000).*
- **Size and shape characterization of short-fiber systems:** Only microscopic image analysis provides unbiased and direct quantitative information *(PABST, BERTHOLD & GREGOROVÁ, submitted).*
- **Rheology of fiber suspensions:** Fiber shape has a direct influence e.g. on effective viscosity. This influence can be quantified *(PABST, GREGOROVÁ & BERTHOLD, submitted).*

Objectives

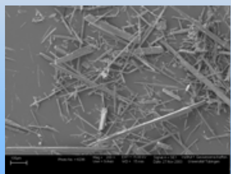
- Determination of the size and shape distribution of a polydisperse short-fiber system by image analysis. Quantification of the "average shape".
- Measuring the effective viscosity of short-fiber suspensions in dependence of the fiber volume fraction via rotational viscometry.
- Fitting the concentration dependence of viscosity and extracting physically meaningful parameters.
- Comparison with the predictions based on the "average shape" obtained from image analysis.

Materials

Two types of wollastonite, WM 45 and HSV 45.



Optical micrograph of wollastonite WM 45.

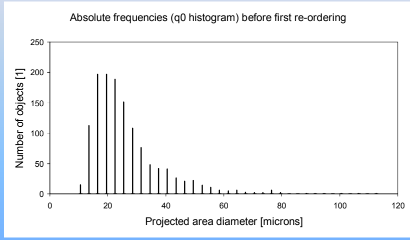


SEM micrograph of wollastonite HSV 45.

Microscopic image analysis 1

- Software: LUCIA G version 4.81 (Laboratory Imaging, Prague, Czech Republic).
- Short-fibers marked manually by rectangles (or five-point ellipses), 1000-1500 objects measured.
- Selected size measures: **Projected area diameter**, minimum and maximum Feret diameter.
- Selected shape measure: **Aspect ratio** (individual aspect ratios calculated from minimum and maximum Feret diameters).
- **Transformation** to **volume-weighted** distributions.

Microscopic image analysis 2



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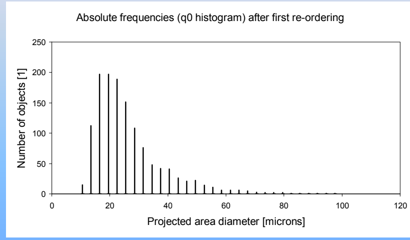
Microscopic image analysis 3



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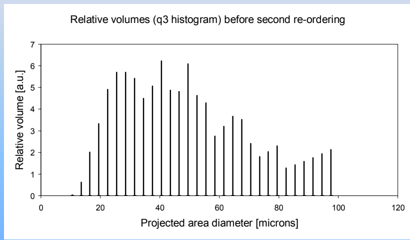
Microscopic image analysis 4



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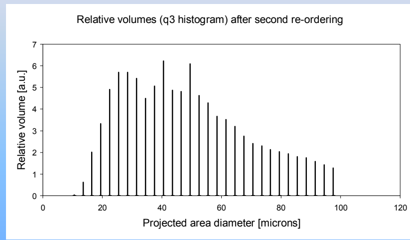
Microscopic image analysis 5



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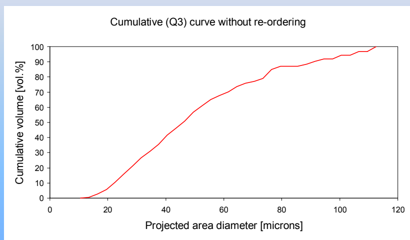
Microscopic image analysis 6



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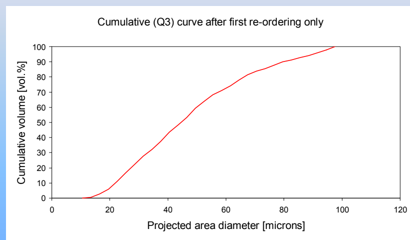
Microscopic image analysis 7



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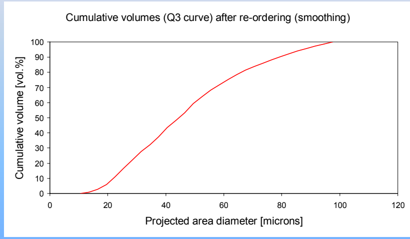
Microscopic image analysis 8



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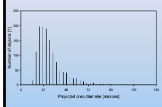
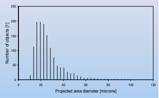
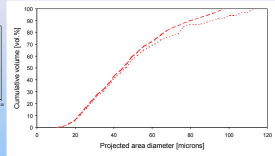
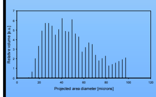
Microscopic image analysis 9

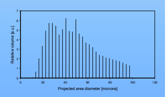


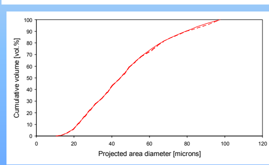




First re-ordering (q_0)







Second re-ordering (q_3)

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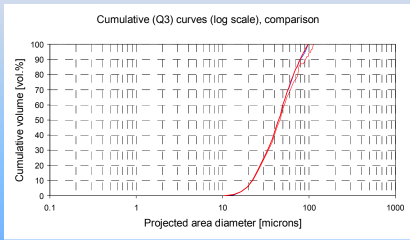
Microscopic image analysis 10



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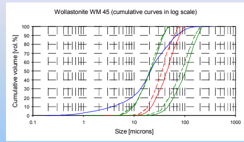
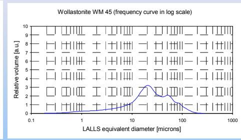
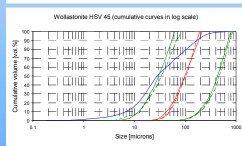
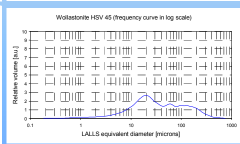
WM 45





HSV 45





Red: projected area diam., green: Feret diam., blue: laser diffraction diam.

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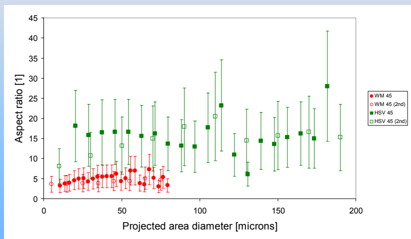
Average aspect ratios: WM 45 approx. 5, HSV 45 approx. 16 (scatter 50 %)



Red circles: WM 45, green squares: HSV 45 (full: 1st operator, empty: 2nd operator)

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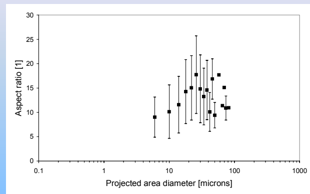
Microscopic image analysis 13



Shape-size dependence curve of prolate (needle-like) particles measured via microscopic image analysis (size class average aspect ratios between 9 and 18, arithmetic average of individual particles approx. 12.5, grand arithmetic average of size class averages approx. 13.1 ± 2.8, median aspect ratio 8.9 ± 0.5)

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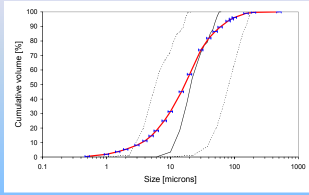
Microscopic image analysis 14



Volume-weighted size distributions (i.e. obtained from the number-weighted size distributions after transformation) of the prolate particle system; dotted curves: minimum (left) and maximum (right) Feret diameter (image analysis), thin full curve: projected area diameter, thick full curve with error bars: laser diffraction diameter

Conclusions – Image analysis

- Although the scatter is large (approx. 50 % within each size class and approx. 25 % among the mean values), **average aspect ratios** are well reproducible and roughly size invariant, approx. 5 for wollastonite WM 45 and approx. 16 for wollastonite HSV 45.
- The transformation procedure applied ("q_0-Q_3 transformation" from number-weighted to volume-weighted particle size distributions) is a generic technique, applicable to any short-fiber system.
- For short-fiber systems **laser diffraction** results are close to the minimum Feret diameter, i.e. significantly **lower than** the projected area diameter determined via **image analysis**.

Suspension rheology – Theory 1

- Relative viscosity: $\eta_r \equiv \frac{\eta}{\eta_0}$
- Intrinsic viscosity: $[\eta] \equiv \lim_{\phi \to 0} \frac{\eta_r - 1}{\phi}$
- Viscosity of **dilute** suspensions (Jeffery-Einstein):

$$\eta_r = 1 + [\eta]\phi$$

- Viscosity of **concentrated** suspensions:

$$\eta_r = \left(1 - \frac{\phi}{\phi_C}\right)^{-[\eta]\phi_C} \quad \text{(Krieger)}$$

$$\eta_r = \left(1 - \frac{\phi}{\phi_C}\right)^{-2} \quad \text{(Maron-Pierce)}$$

(viscosity η , viscosity of the suspending medium η_0 , volume fraction ϕ , critical volume fraction ϕ_C)

Suspension rheology – Theory 2

- Dependence of the **intrinsic viscosity** on the aspect ratio $[\eta](R)$ (Brenner formula, theoretically sound)

$$[\eta] = 5Q_1 - \frac{15}{4}Q_2\langle \sin^2\theta \rangle - \frac{5}{4B}(3Q_2 + 4Q_4)\langle \sin^2\theta \cos 2\phi \rangle + \frac{15}{2BP}(3Q_2 + 4Q_3)\langle \sin^2\theta \sin 2\phi \rangle$$

The five material constants B, Q_1, Q_2, Q_3, Q_4 are all functions of the aspect ratio and P is the rotary Péclet number, i.e. the ratio between shear rate and rotary Brownian diffusion coefficient (a function of shape and size). For weak Brownian motion (P>>1 and P>>R^3) the following approximate expression holds:

$$[\eta]_\infty = 2.5 + 0.123(R-1)^{0.925}$$

Suspension rheology – Theory 3

- Dependence of the **critical volume fraction** on the aspect ratio $\phi_C(R)$ (Kitano relation, purely empirical)

$$\phi_C = 0.54 - 0.0125 \cdot R$$

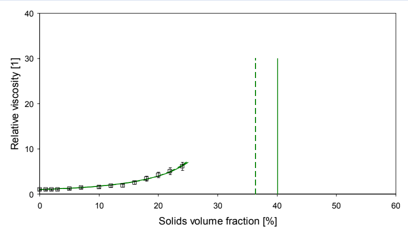
- **Rotary Péclet numbers** (shear rate 1000 s^{-1}, minimum Feret diameter 10 µm, temperature 25 °C): **$6.2 \cdot 10^9$** and **$12.4 \cdot 10^9$** for wollastonites WM 45 (average aspect ratio 5) and HSV 45 (aspect ratio 16) in 60 wt.% sugar solution (density 1.285 g/cm^3, viscosity 43 mPas) → **weak Brownian motion**.

Suspension rheology – Experimental

- **Suspensions:** Wollastonites (density 2.9 g/cm^3) WM 45 and HSV 45 in 60 wt.% sugar solution (density 1.285 g/cm^3, viscosity 43 mPas), prepared by ultrasonication. Sedimentation times increased by a factor of approx. 50 compared to pure water.
- **Viscometric measurements:** Rotational viscometer RV1 (Haake, Germany) with coaxial cylinder system Z41. Schedule: 60 s ramp up, 30 s hold at a shear rate of 1000 s^{-1}, 60 s ramp down. Viscosity measured at 1000 s^{-1}. The flow behavior is close to Newtonian.

Suspension rheology – Results 1

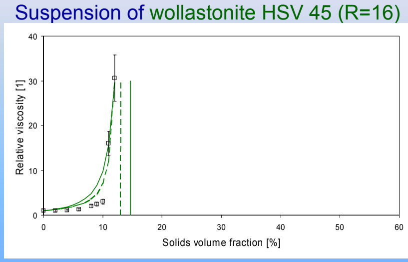
Suspension of wollastonite WM 45 (R=5)



Measured values (empty squares, error bars), Krieger fit (dashed line), Maron-Pierce fit (full line)

Suspension rheology – Results 2

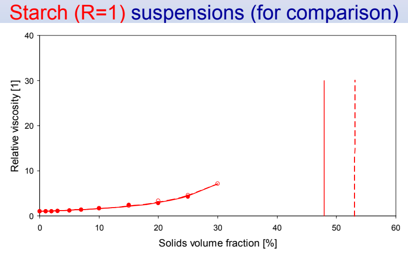
Suspension of wollastonite HSV 45 (R=16)



Measured values (empty squares, error bars), Krieger fit (dashed line), Maron-Pierce fit (full line)

Suspension rheology – Results 3

Starch (R=1) suspensions (for comparison)



Measured values (circles, full: corn, empty: wheat), Krieger fit (dashed), Maron-Pierce fit (full line)

Suspension rheology – Results 4

Critical volume fraction and intrinsic viscosity;
fit parameters obtained via
the Krieger relation (left) or the Maron-Pierce relation (right)

Material	Aspect Ratio	ϕ_C	$[\eta]$
Starch	1	0.531	4.44
WM 45	5	0.363	4.70
HSV 45	16	0.130	10.2

Material	Aspect Ratio	ϕ_C	$[\eta]_{est.}$
Starch	1	0.479	4.18
WM 45	5	0.401	4.99
HSV 45	16	0.147	13.6

$$\eta_r = \left(1 - \frac{\phi}{\phi_C}\right)^{-[\eta]\phi_C}$$

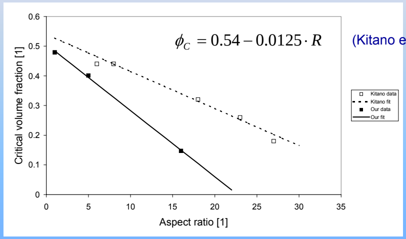
Krieger relation

$$\eta_r = \left(1 - \frac{\phi}{\phi_C}\right)^{-2}$$

Maron-Pierce relation

Suspension rheology – Results 5

Comparison of Kitano et al. data and fit with our data and fit



(Kitano et al. 1981)

$\phi_C = 0.51 - 0.0223 \cdot R$ (Pabst et al. 2004)

Conclusions - Suspension rheology 1

- Experimentally determined **intrinsic viscosities** (4.3, 4.8 and 11.9 for particle systems with average aspect ratios 1, 5 and 16 respectively) are significantly **higher than theoretically predicted**, which are 2.5, 2.8 and 3.9, respectively (Brenner formula).
- This is in agreement with the empirical finding occurring in the literature that in practice the Batchinski formula

$$\eta_r = 1 + 4.5\,\phi$$

"works better" than the (theoretically well founded) Einstein formula

$$\eta_r = 1 + 2.5\,\phi$$

- Probable reason: electrostatic (not steric) interactions

Conclusions - Suspension rheology 2

- Experimentally determined **critical volume fractions** (51 %, 38 % and 14 % for particle systems with average aspect ratios 1, 5 and 16 respectively) are significantly **lower than expected**, which are 53 %, 48 % and 34 %, respectively (Kitano et al.).
- This shows that the frequently cited Kitano relation with the original values given by Kitano et al.

$$\phi_C = 0.54 - 0.0125 \cdot R$$

need not be useful for real systems. Being purely empirical a more general validity cannot be expected.
- For our wollastonite suspensions we find

$$\phi_C = 0.51 - 0.0223 \cdot R$$

- Probable reason: polydispersity in shape (not in size)

Acknowledgement

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- Project “Tvorba předmětu Charakterizace částic a částicových soustav“, Czech Ministry of Education, Youth and Sports (Grant FRVŠ 674 / 2007 / F1b).

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Selected references:

[1] Pabst W., Kuneš K., Havrda J., Gregorová E.: *J. Eur. Ceram. Soc.* **20** (2000), 1429.
[2] Berthold C., Klein R., Lühmann J., Nickel K. G.: *Part. Part. Syst. Charact.* **17** (2000), 113.
[3] Pabst W., Kuneš K., Gregorová E., Havrda J.: *Brit. Ceram. Trans.* **100** (2001), 106.
[4] Pabst W., Kuneš K., Gregorová E., Havrda J.: *Key Eng. Mater.* **206-213** (2002), 743.
[5] Pabst W., Berthold C., Gregorová E.: *J. Eur. Ceram. Soc.* **26** (2005), 1121.
[6] Pabst W., Gregorová E., Berthold C. *J. Eur. Ceram. Soc.* **26** (2005), 149.
[7] Pabst W., Berthold C., Gregorová E.: *J. Eur. Ceram. Soc.* **27** (2007), 1759.