AVEKA Group

PARTICLE PROCESSING AND THE VALUE OF CHARACTERIZATION

DECEMBER 12, 2018

PRESENTED BY: WILLIE HENDRICKSON, CEO & FOUNDER
Presentation Outline

• Overview of AVEKA
• Reasons for Characterization
• Types of Characterization Methods to Consider
• Examples of Characterization Challenges and Some Solutions
• Conclusions
AVEKA Group Overview

- Particle technology company focused on contract manufacturing
- Spin-off of 3M in 1994
- Comprised of 5 separate companies
- ISO certifications / food-grade certifications
- Currently 290 employees
AVEKA’s Vision
be the recognized leader in
innovative manufacturing solutions
for particle technology

AVEKA’s Mission
be the leader in particle processing
by providing our customers with custom solutions,
quality manufacturing and excellent customer service
The AVEKA Group

AVEKA Inc
- 75 people
- Corporate Headquarters
- R&D, Manufacturing, Specialty Process Suites

AVEKA Manufacturing
- 96 people – Fredericksburg, Iowa
- Large scale manufacturing
- Spray Drying, Hammer Milling, Fluid Bed Drying, Tumble Coating, Agglomeration

Cresco Food Technologies
- 50 people – Cresco, Iowa
- Food Processing
- Spray Drying, Prilling, Drum Drying, Extraction, Wet Blending

AVEKA Nutra Processing
- 40 people – Waukon Iowa
- Value Added Food Processing
- Spray Drying, Roll Drying, Microfiltration/Nanofiltration, Specialty Separations

AVEKA CCE Technologies
- 15 People – Cottage Grove, Minnesota
- Industrial Materials, Abrasives, Ceramics, Minerals
- Jet Milling and Classification
Particle Characterization

Particle size analysis
- Particles 1 nm to 2+ mm
- Particle size distribution (PSD)
- Sonic sieving
- Rototap

Imaging
- Optical microscopy
- Scanning electron microscopy (SEM)

Surface area analysis

True density analysis
- Helium pycnometry

Formulation analysis
- High performance liquid chromatography (HPLC)
- Thermogravimetric analysis (TGA)
- Spectrophotometer
- Differential scanning calorimetry (DSC)

Flow characteristics
- Freeman FT4
- Zeta potential analysis (ZP)
- Rheological analysis
- Moisture and solids analysis (MSA)
- Karl Fisher
Reasons for Characterization

• Scientific Curiosity
• IP Development and Protection
• Process Control/Understanding
• Product Control
• Quality Control
• Impurity Analysis
Characterization Methods

- Visual Inspection (color, flow, size, uniformity, etc.)
- Mass Balance Measurements
- Optical Microscopy
- Particle Size/Shape
- Particle Flow
- Chemical Characterization
- Surface Area
- Electrical Characteristics
Classification by Screening

Challenge: Rapid and efficient screening of powders less than 200 microns

Screening at 74 μm of encapsulated fragrance particles using a 30 inch Screener

<table>
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<th>Rate (lbs./hr.)</th>
<th>Ultrasonics</th>
<th>Overs (%)</th>
<th>Product (%)</th>
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<tr>
<td>159</td>
<td>yes</td>
<td>30</td>
<td>70</td>
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</table>
Ultrasonic Screening
Quality Control

Process:
• Crushing and ball milling ceramic blocks
• Followed by screening

Specifications (microns)
• $d_{10} < 1.7$
• $d_{50} = 4-15$
• $d_{90} = 15-40$
Ceramic Particle Size Distribution

**HORIBA LA-930**

**Aveka Characterization Lab**
Paul Verbanac, Lab Manager
2045 Wooddale Drive
Woodbury, MN 55125
Phone: (651) 330-1279

**% on Diameter**
- 98.66% (0.4942μm)
- 20.00% (0.6771μm)
- 20.00% (0.8050μm)
- 20.00% (2.5637μm)
- 20.00% (3.4267μm)

**Diameter (μm)**

**Frequency (%)**

**Underline (%)**

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<th>No.</th>
<th>Diameter (μm)</th>
<th>Freq. %</th>
<th>Under %</th>
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<tr>
<td>1</td>
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<tr>
<td>20</td>
<td>0.54</td>
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<td>21</td>
<td>0.55</td>
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**NOTE:** The above data represents the ceramic particle size distribution measured by the AVEKA LA-930 laser diffraction particle size analyzer.
Ceramic Particle Size Distribution After Screening

<table>
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<tr>
<th>Diameter (μm)</th>
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<td>0.020</td>
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<tr>
<td>0.050</td>
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<tr>
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AVeka Characterization Lab
Paul Verhees, Lab Manager
2045 Woodside Drive
Woodbury, MN 55125
Phone: (651) 730-1729

HORIBA LA-930
For Windows (TM) [CESA08LA930] Ver 3.49

<table>
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<tr>
<th>Source</th>
<th>Sample Name</th>
<th>Material</th>
<th>Screening</th>
<th>Carrying</th>
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<tr>
<td>JMG409</td>
<td>FineAfter</td>
<td>Ball Mill Fine Corindite</td>
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<table>
<thead>
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<th>% on Diameter</th>
<th>Diam. (μm)</th>
<th>Frequency (%)</th>
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<td>2.000 000</td>
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<table>
<thead>
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<tr>
<td>5.000</td>
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</table>
Results of Screening

Size Distributions Exactly the Same
• Some product was usable
• Some product was not usable

Why?
• Small quantity of unmeasured large particles

Solution
• Wet screening and microscopic evaluation
Jet Milling vs. Ball Milling of Zirconia Sand

Jet Milling

- <10%: 2.449 μm
- <25%: 4.120 μm
- <50%: 6.671 μm
- <75%: 9.133 μm
- <90%: 10.75 μm

Ball Milling

- <10%: 1.796 μm
- <25%: 3.191 μm
- <50%: 6.317 μm
- <75%: 10.25 μm
- <90%: 13.66 μm

Objective: Minimization of Fines
Jet Milling vs. Ball Milling of Zirconia Sand

Starting Zirconia Sand

Jet Milled Zirconia

Ball Milled Zirconia
Glass Bead Classifications and Yields

Glass Beads Starting Material

Glass Bead Classification (2 Versions)

<table>
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<tr>
<th>Starting Glass</th>
<th>&lt;10%</th>
<th>&lt;25%</th>
<th>&lt;50%</th>
<th>&lt;75%</th>
<th>&lt;90%</th>
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<tr>
<td></td>
<td>19.01 μm</td>
<td>25.08 μm</td>
<td>33.10 μm</td>
<td>41.56 μm</td>
<td>48.29 μm</td>
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<tr>
<td>Classification (red)</td>
<td>23.95 μm</td>
<td>28.22 μm</td>
<td>35.82 μm</td>
<td>43.94 μm</td>
<td>50.41 μm</td>
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<tr>
<td>Classification (green)</td>
<td>24.95 μm</td>
<td>29.05 μm</td>
<td>34.89 μm</td>
<td>41.96 μm</td>
<td>48.47 μm</td>
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Objective: Increase yield after classification
Glass Bead Classification and Yields

Starting Beads

Broad Cut (24-50 μm)  
73% Yield

Narrow Cut (25-48 μm)  
43% Yield
Jet Milling and Classification of Polymer

Jet Milled Polymer

Jet Milled and Classified Polymer
Jet Milling and Classification of Polymer

Starting Material

Jet Milled and Classified Polymer

Jet Milled Polymer
Jet Milling and Separation of Starch and Protein

Raw Pea Flour

Conc. Pea Starch

Conc. Pea Protein
Jet Milling and Air Separation of Starch & Protein

Raw Pea Flour

Conc. Pea Protein

Conc. Pea Starch
Spheroidizing

Particle size
- remains the same

Processing Rate
- up to 20 kg/hour

Atomization Air Temp
- up to 650°C

Industrial materials

Ideal Materials
- Thermoplastics, pigments
Spheroidizing
MAIC: Magnetically Assisted Impact Coating

Particle Surface Treatment:
- Add flow agents (silica)
- Coat with solids (TiO₂, ZnO)
- Distribute liquids (silanes)
  - US Patent 5,962,082
- Can be used for many applications and industries
  - Agriculture materials, cosmetics, pigments, catalysts
MAIC Unit
Magnetically Assisted Impact Coating

Particles to be modified
• Modifying material

Feed system

Screens and magnets

Magnetic coils

Coated particles
Experimental Parameters

Materials:
- Citric acid monohydrate jet milled to 5 μm or Corn Starch
- Aerosil 200 Pharma, untreated fumed silica with 12 nm primary particle size

Samples:

<table>
<thead>
<tr>
<th></th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>A</th>
<th>G</th>
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<td>MAIC</td>
<td>MAIC</td>
<td>MAIC</td>
<td>V-blended</td>
<td>V-blended</td>
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</table>

Sample Preparations:

Citric acid or corn starch blended with 0-2 wt. % fumed silica in V-blender

Passed through MAIC or Set Aside
Flow Measurement Results for Citric Acid

- Clear decreases in BFE with increasing % silica
- Marked decrease between the raw and MAIC treated sample (0% (w/w) silica)
- At equal silica loadings, MAIC samples show lower BFE
- 0.5% MAIC and 2.0% V-blend near equal
Comparing MAIC to V-Blending

\[ BFE = A \times (1 + B e^{-\left(\frac{x}{C}\right)^{0.32}}) \]

Thanks to P. Mort, P&G
Citric Acid – Short Term

- MAIC processing initially yields a lower BFE in all cases
- Silica addition via v-blending does not improve BFE
- The mean difference between v-blending and MAIC for each silica loading level is significant at $p < .0001$. 

![Bar chart showing BFE (ml) for different silica loadings and processing methods.](chart.png)
**Citric Acid – Long Term**

- MAIC-applied silica on citric acid maintains lower BFE than corresponding v-blend
- Addition of more silica does show improvement for MAIC samples ($p < .0001, r^2 = .64$)
- Divergent behavior observed for MAIC-processed citric acid without silica
- The mean difference between v-blending and MAIC for each silica loading level is significant at $p < .0001$, except for 0% silica ($p = .170$). 

![Graph showing BFE (mL) for different silica loading levels and comparison between v-blending and MAIC processes over 2 years.](image)
Cornstarch SEM Images

Cornstarch, 5% silica (MAIC), fresh

Cornstarch, 5% silica (MAIC), 1 year later
Cornstarch – Short Term

- Like citric acid, MAIC-processing initially yields a lower BFE in all cases
- The addition of small amounts of silica does not lower BFE
- The mean difference between v-blending and MAIC for each silica loading level is significant at $p < .05$
Cornstarch – Long Term

- After 9 months, the differences between MAIC and v-blending cannot be observed
- Processing effects appear to have worn off,
- Addition of silica does not appear to lower BFE except for the highest loading levels (5%)
Spray Drying of Materials with Waters of Hydration

Interested in Hydrated Inorganic and Polymer Precursors for Novel Material Production

\[ \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \]
- For alumina based ceramics

\[ \text{Na}_2\text{Succinate} \cdot 6\text{H}_2\text{O} \]
- For polyester type polymers

Typical drying conditions of 95 °C
Particle Size Distribution (PSD):
Spray Dried Aluminum Sulfate NX326-13-01

<table>
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<tr>
<th>Remarks 1</th>
<th>IPA</th>
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<td>Mean Size</td>
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<td>Median Size</td>
<td>5.62878(µm)</td>
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<td>Std.Dev.</td>
<td>4.7652(µm)</td>
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<td>Mode Size</td>
<td>5.4795(µm)</td>
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<td>S.P.Area</td>
<td>13926(cm²/cm³)</td>
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<tr>
<td>Diameter on Cumulative %</td>
<td>(1)5.000 (%) - 1.6910(µm)</td>
</tr>
<tr>
<td></td>
<td>(2)10.00 (%) - 2.2327(µm)</td>
</tr>
<tr>
<td></td>
<td>(3)50.00 (%) - 5.6288(µm)</td>
</tr>
<tr>
<td></td>
<td>(4)90.00 (%) - 13.6195(µm)</td>
</tr>
<tr>
<td></td>
<td>(5)98.00 (%) - 19.9238(µm)</td>
</tr>
</tbody>
</table>

Cumulative % on Diameter:
(1)10.00 (µm) - 78.407(%)  
(2)25.00 (µm) - 99.466(%)  
(3)50.00 (µm) - 100.000(%)  
(4)75.00 (µm) - 100.000(%)  
(5)100.0 (µm) - 100.000(%)  
(6)150.0 (µm) - 100.000(%)  
(7)180.0 (µm) - 100.000(%)  

D_{10} = 2.23 µm  
D_{50} = 5.63 µm  
D_{90} = 13.6 µm
Spray Dried Anhydrous Aluminum Sulfate

10,000 X

10,000 X
Spray Dried Anhydrous Na Succinate
Ambient Aged Spray Dried Materials

Anhydrous Sodium Succinate

Hydrated Sodium Succinate
Interior of Spray Dried Anhydrous and Hydrated Na Succinate

Anhydrous Na Succinate

Rehydrated Na Succinate
# Corn Bran Overview

## Corn Bran Composition
- Starch: 1-10%
- Protein: 1-8%
- Oils: 0-2%
- Ash: 1-6%
- Water: 1-10%

## Cellulose/Hemicellulose/Lignin Composition
- Cellulose: 25-30%
- Hemicellulose: 60-70%
- Lignin: 1-6%
Material Characteristics

Cellulose
- Polymer of glucose
- Insoluble in common solvents
- Highly crystalline

Hemicellulose
- Polymer of Xylose
- Soluble in caustic
Material Characteristics

Lignin

- Cross-linked aromatic polymer
- Soluble in caustic
- Highly colored
Fiber Structure
Cellulose Images
Compostional Analysis

TGA
• Heat at constant rate
• Use high resolution option to measure weight changes
• Heat to 800 °C

Chemical Dissolution
• Wash with detergent and water (water solubles)
• Wash with dilute sulfuric acid (hemicellulose)
• Wash with conc. sulfuric acid (cellulose)
• Ash at 500 °C (lignin)
• Remainder after ashing (ash)
TGA of Cellulose and Hemicellulose

Wood Cellulose

Hemicellulose
TGA of Corn Bran and Purified Cellulose
# TGA Results

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<tr>
<th>Sample</th>
<th>% Cellulose</th>
<th>Cellulose Decomp Temp</th>
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<td>Cellulose</td>
<td>100</td>
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<td>20/80 (H/C)</td>
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<td>309.83</td>
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<tr>
<td>40/60 (H/C)</td>
<td>60</td>
<td>316.89</td>
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<tr>
<td>50/50 (H/C)</td>
<td>50</td>
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<td>80/20 (H/C)</td>
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<td>20/80 (S/C)</td>
<td>80</td>
<td>300.75</td>
</tr>
<tr>
<td>40/60 (S/C)</td>
<td>60</td>
<td>305.8</td>
</tr>
<tr>
<td>50/50 (S/C)</td>
<td>50</td>
<td>306.80</td>
</tr>
<tr>
<td>65/35 (S/C)</td>
<td>35</td>
<td>311.79</td>
</tr>
<tr>
<td>80/20 (S/C)</td>
<td>20</td>
<td>316.34</td>
</tr>
</tbody>
</table>
TGA Results

Hemicellulose Added to Cellulose

Starch Added to Cellulose
Impurity Characterization

Optical Image of Impurity

Background Information

- Found by customer in product
- Potential for recall
- Process analysis done and potential contaminant determined to be
  - Zip tie from equipment
  - Adhesive from customer’s bag
- Characterization critical for understanding
Impurity Characterization

TGA Comparison

DSC Comparison
Impurity Characterization

TGA Comparison

DSC Comparison
Summary

- Characterization is critical to meet product and customer needs
- Multiple methods should be considered for most complete understanding
- It is hard to analyze too much

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