10th World Flexible Intermediate Bulk Container Conference
Marriott Hotel, Amsterdam, NL May 2-3, 2017

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Calcium Carbonate in FIBC's

A Detailed View on the Specification, Utilization and Performance of $CaCO_3$ in FIBC Manufacture

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Mission Statement

Key questions this presentation will try to address:

1. ***What is $CaCO_3$,and why is it in my FIBC***

2. ***Are all $CaCO_3$ additives created equal?***
3. ***How do I differentiate $CaCO_3$ additives?***
4. ***How is $CaCO_3$ introduced into my FIBC?***
5. ***How do I know much is in my FIBC and is there a maximum level?***

Outline: Understanding Calcium Carbonate

- **Part I: Calcium Carbonate: Origins, Sources and Forms**
  - Minerals and mineral forms
  - Organogenic sedimentation of $CaCO_3$
  - $CaCO_3$ Production
- **Part II: Applications and Properties of Calcium Carbonate**
  - Applications
  - Physical Properties
  - Understanding Particle Size Distribution
- **Part III: Calcium Carbonate in FIBC Materials**
  - Understanding Stress-Strain
  - Effect of $CaCO_3$ content in PP for FIBCs (Experimental Data)
  - Testing for $CaCO_3$
- **Part IV: Summary**

Part I

Calcium Carbonate: Origins, Sources and Forms of the Mineral

Additives

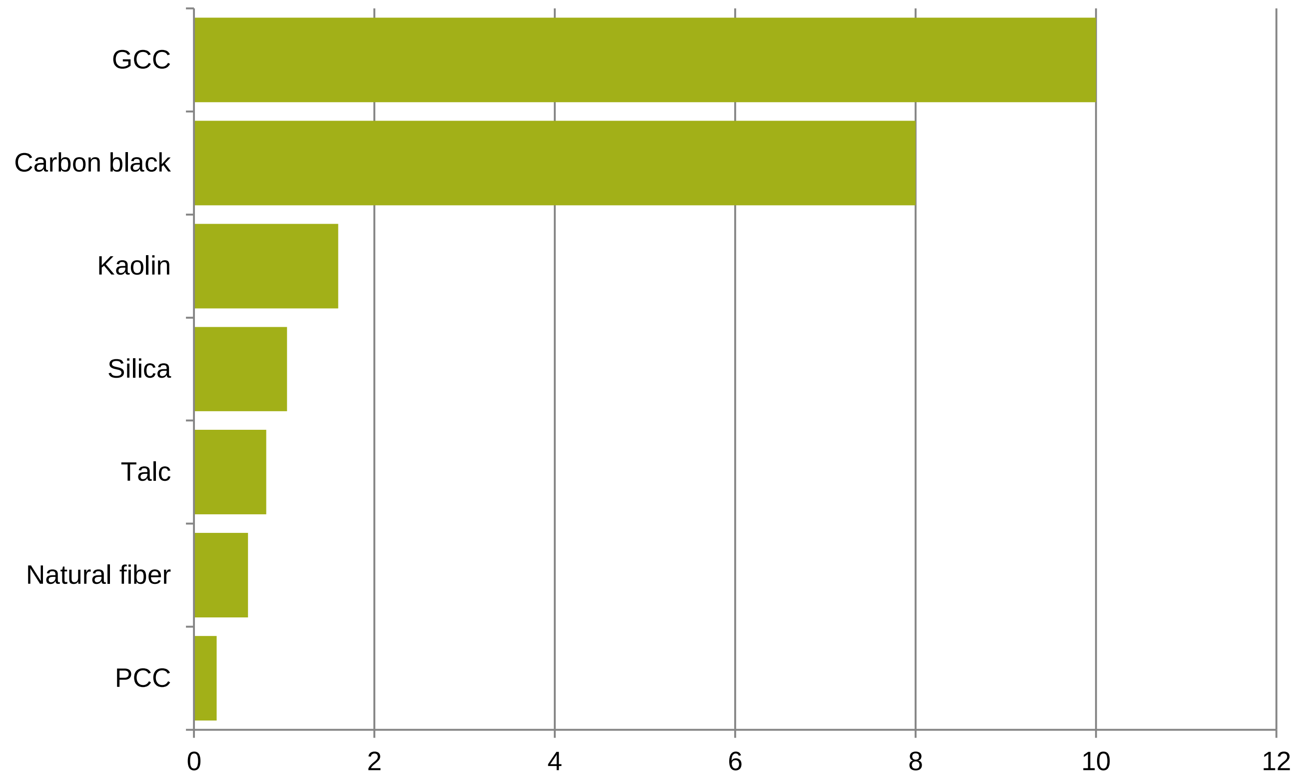
- Additives are special ingredients which when used in small quantities will impart an improved characteristic to a product or process.
- Some examples where additives are useful:
  - Food (taste, texture, appearance)
  - Chemicals (nucleation, reaction time, heat capacity)
  - Plastics (color, strength, flexibility)

Minerals Used as Additives

- Alumina
- Andalusite
- Ball Clay
- Bentonite
- Bauxite
- Calcium Carbonate
- Carbon Black
- Clinoptilolite
- Cordierite
- Diatomaceous Earth
- Dolomite
- Feldspar
- Graphite
- Kaolin
- Magnesite
- Mica
- Olivine
- Perlite
- Silica
- Silicon Carbide
- Vermiculite
- Zirconia

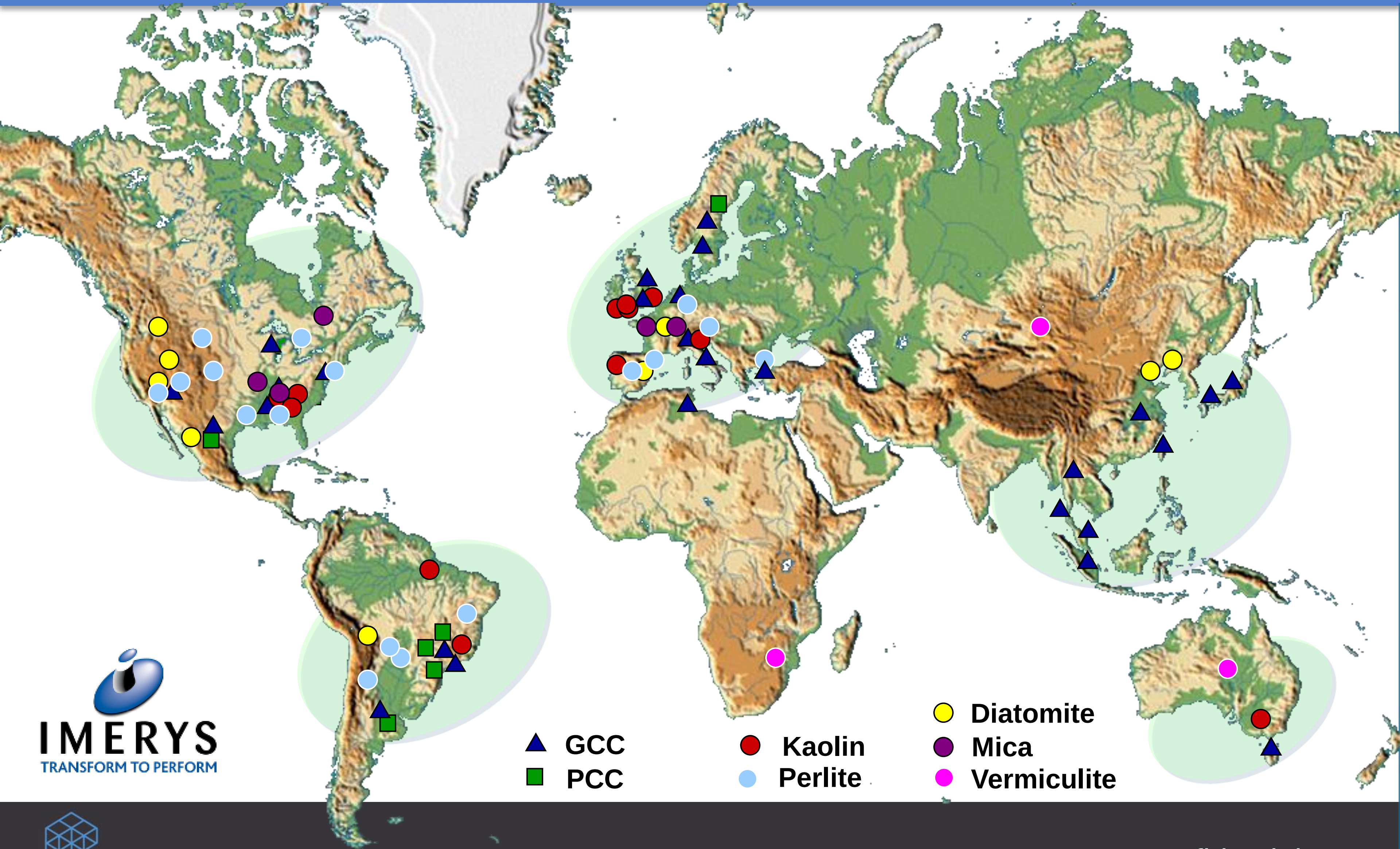
Global Mineral Production

Metric Tons per year x10^6



Source: (AMI 2007+Imerys)

Global Mineral Production



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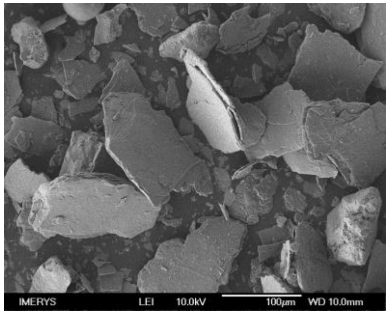
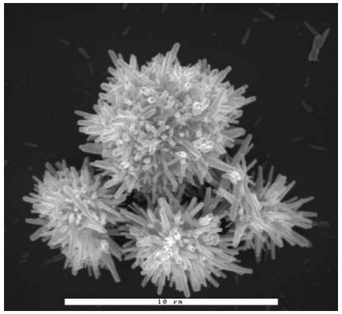
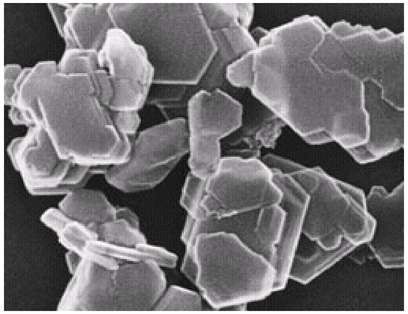
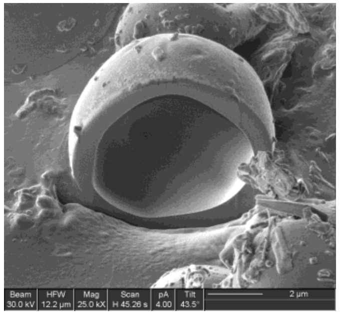
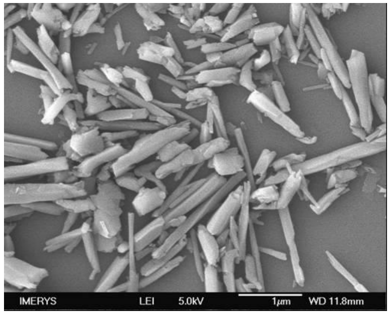
Mineral Particle Morphologies

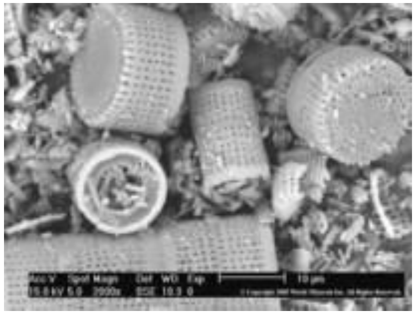


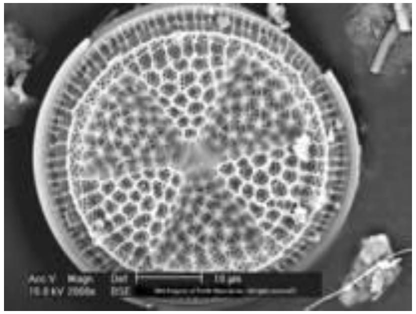


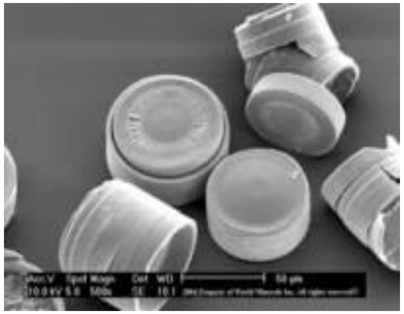












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Source: Imerys

Some Typical Mineral Forms

Kaolin

Ball Clay

Diatomite

Precipitated $CaCO_3$

Ground $CaCO_3$

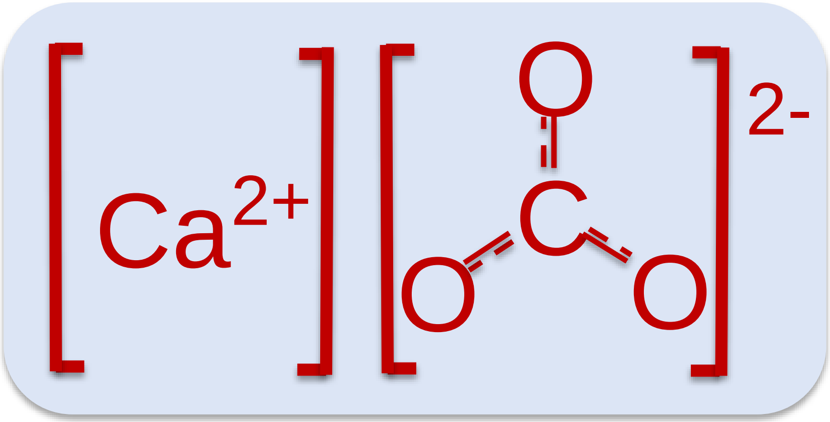
Mica

Perlite

Vermiculite

What is Calcium Carbonate?

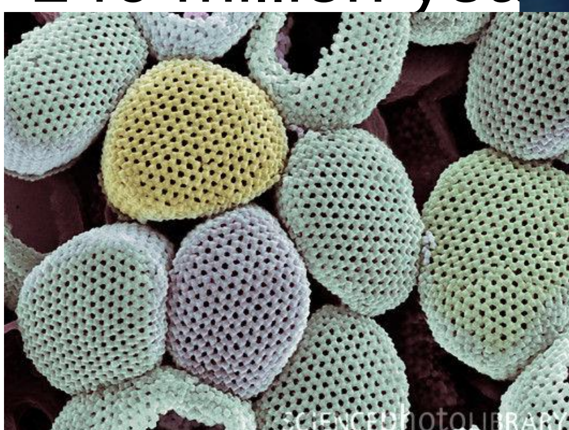
- Calcium Carbonate ($CaCO_3$) is composed of rock forming minerals
  - Calcite
  - Aragonite
  - Vaterite

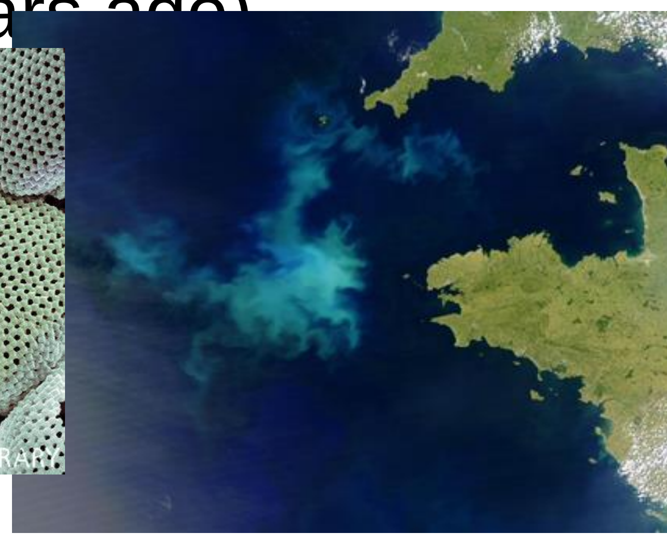


- $CaCO_3$ is a mineral ubiquitous in nature
  - Accounts for 4% of the Earth's crust
  - Water, plants and animals contain large amounts of $CaCO_3$

Calcium Carbonate – from the beginning

Almost all of the World's calcium carbonate reserves originate from the deposition of the skeletons from billions of **microscopic marine organisms** at the bottom of the warm shallow seas of the Cretaceous period (approximately 65 – 140 million years ago)



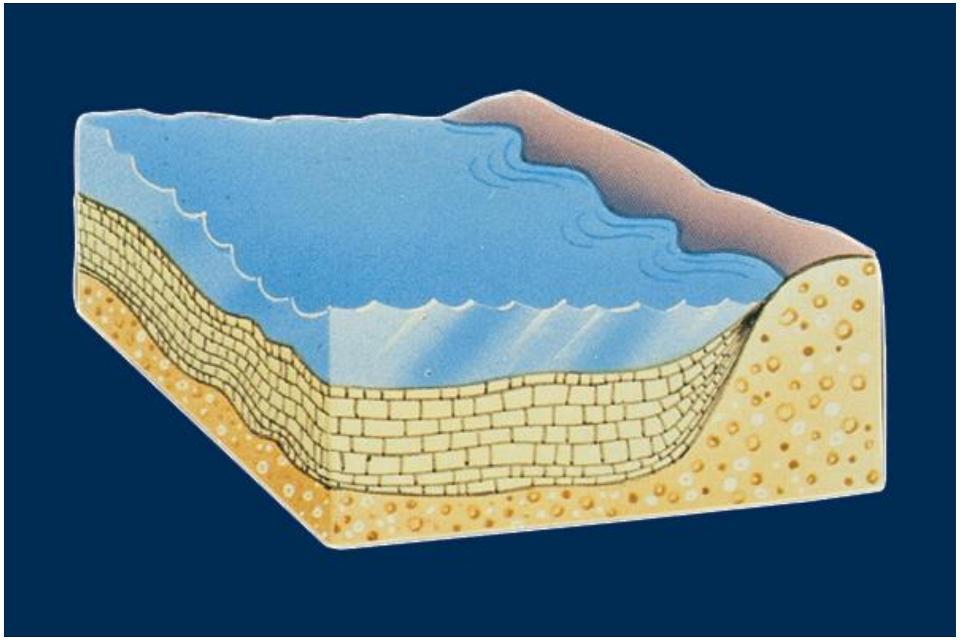


Calcium Carbonate Formation

- Rocks formed from of material of **organic origin**
  - Sedimentation
  - Deposition
  - Cementation (compaction)

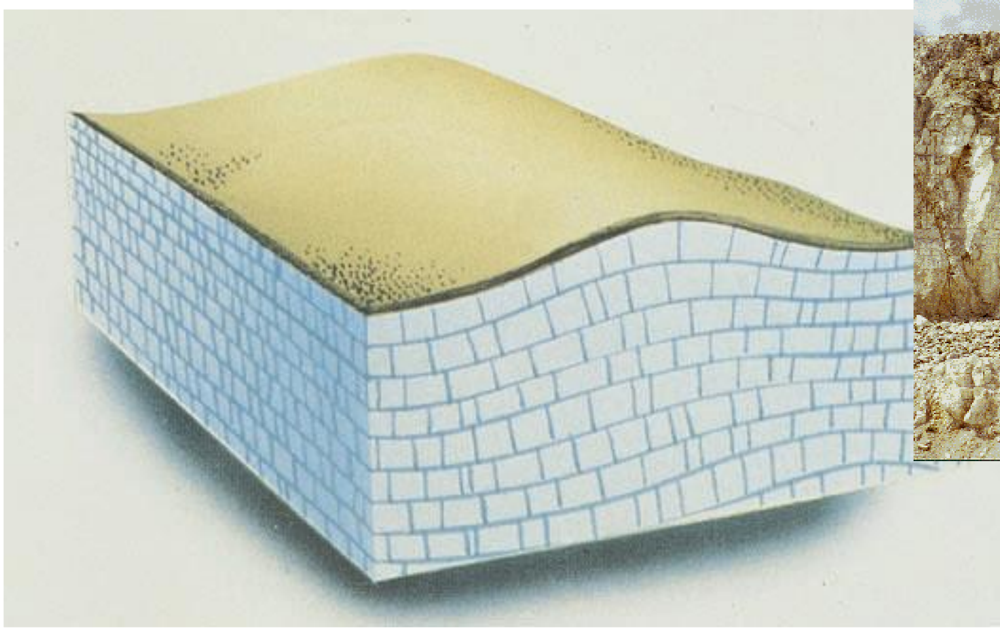
Calcium Carbonate – Sedimentation

- **Organogenic Sedimentation**
  - Sedimentation of the marine organism skeletons occurs in a warm shallow sea



Calcium Carbonate – Chalk

- Geological movements combined with the drying of oceans leaves chalk deposits.
- Clays and soil components are deposited with time, some may permeate into chalk.



Source: Imerys

Calcium Carbonate – Chalk

Spherical body made up of **calcite platelets** with an aspect ratio of about 3:1

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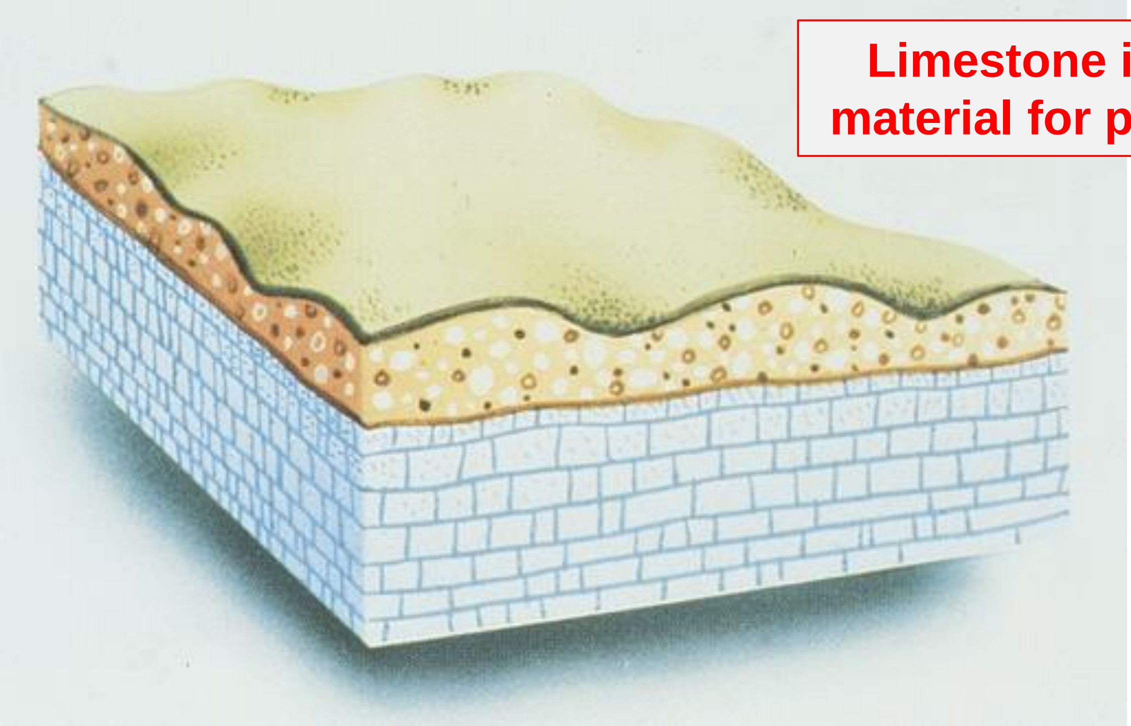
Source: Imerys

Calcium Carbonate – Limestone

Minor compaction by late sediments and chalk becoming harder with formation of flints. Some **compaction** occurs to give harder limestone.

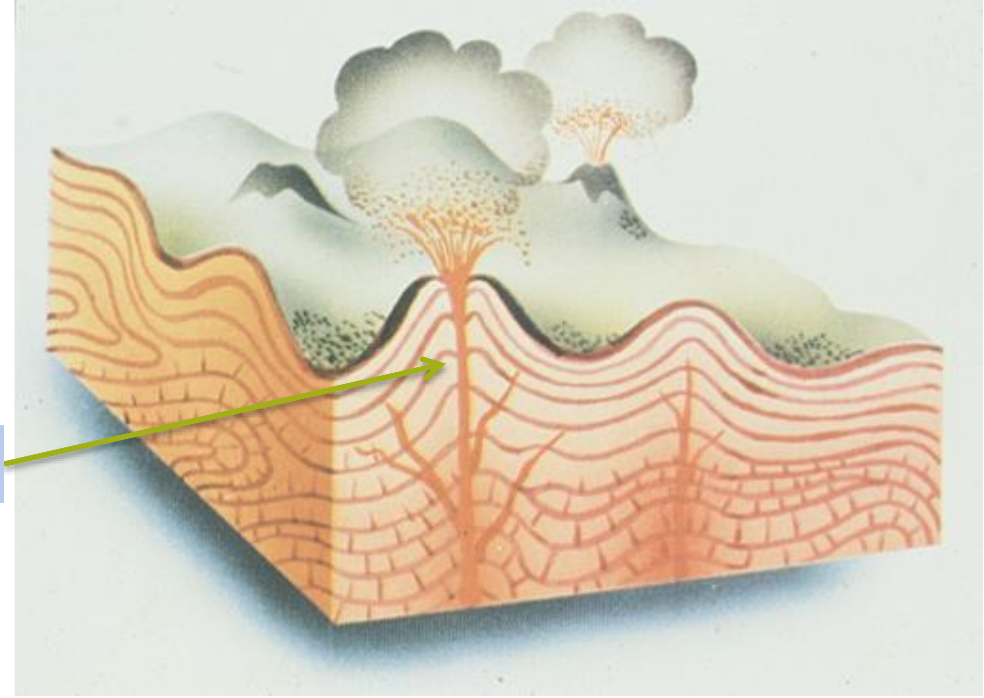


Limestone is the source material for producing PCC

Calcium Carbonate – Marble

Metamorphosis
Volcanic activity leads to localized melting of calcium carbonate deposits that subsequently **re-crystallize** into marble

Marble formed



Calcium Carbonate – Marble

- Marble does not show the same skeletal remains as chalks, as a result of the re-crystallization process

- Marble is typically the source for producing high quality ground calcium carbonate (GCC)

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Source: Imerys

Production Process of Calcium Carbonate

$CaCO_3$ is produced in two distinct forms

- Ground Calcium Carbonate (GCC)

Ground $CaCO_3$

- Precipitated Calcium Carbonate (PCC)

Precipitated $CaCO_3$

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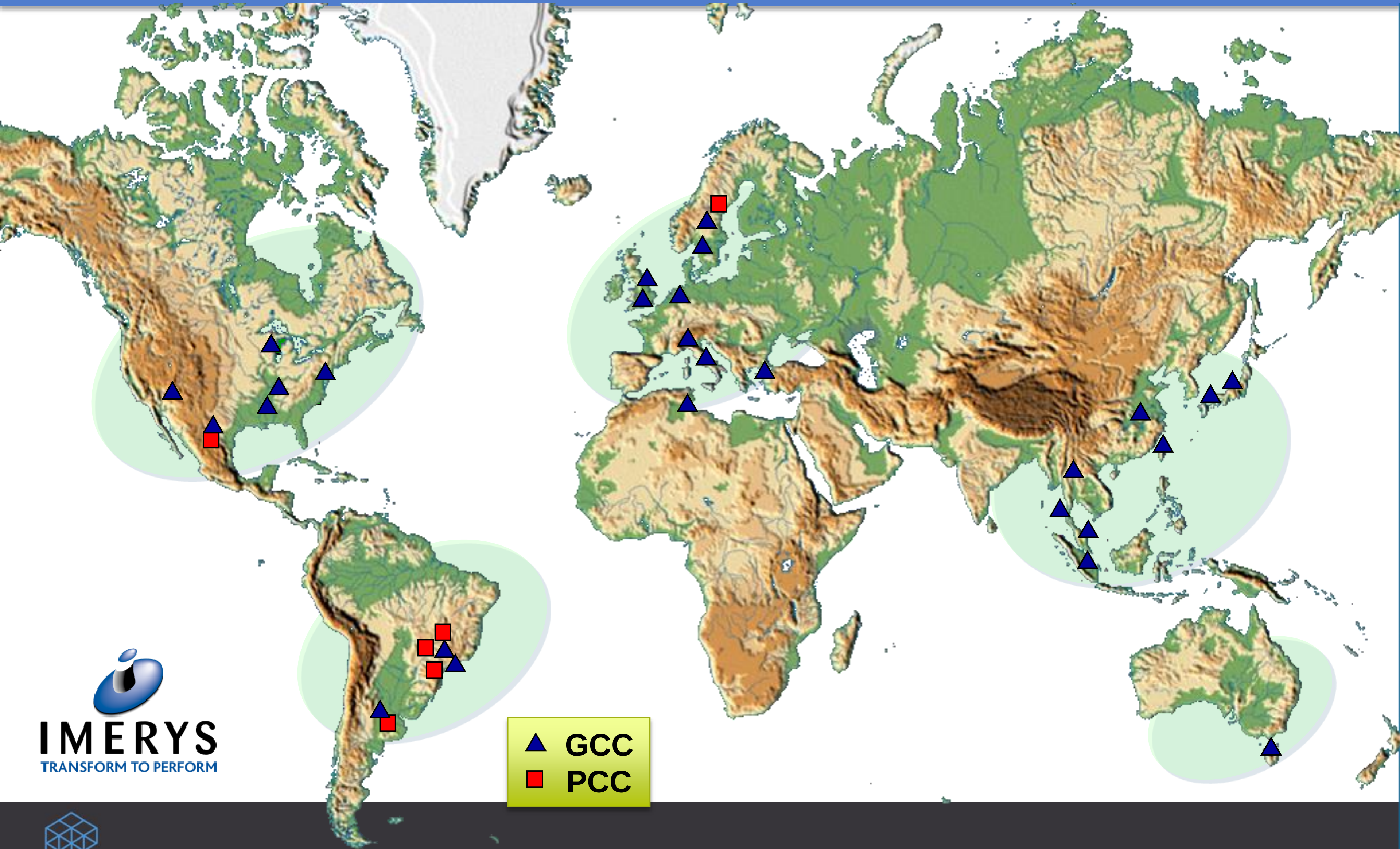
Photos: Imerys

Where CaCO3 is Produced

- Extraction is limited to sites where the purity and uniformity of the deposits are greatest
- Locations
  - North America
  - South America
  - Europe
  - Asia

GCC and PCC (Imerys locations)



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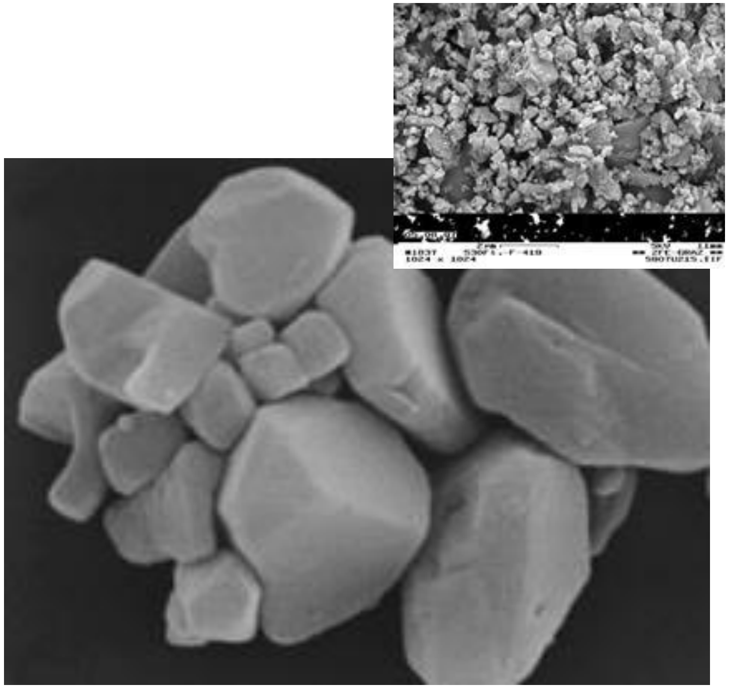
Two Basic Forms of $CaCO_3$

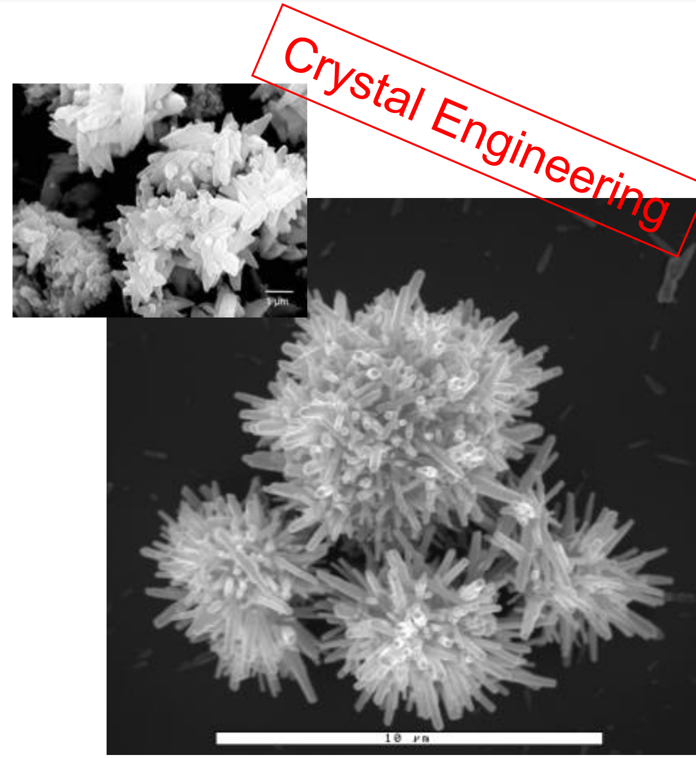
- Ground Calcium Carbonate (GCC)
  - Raw mineral extracted from high purity quarries (typically marble)
  - Crushing, washing and particle sorting
  - Mechanical particle sizing (grinding)
  - Stearic acid treatment (surface tension)



Photos: Imerys

Two Basic Forms of $CaCO_3$

- Precipitated Calcium Carbonate (PCC)
  - Calcination of limestone to produce CaO (lime)
  - Lime is slaked with water
  - Reacted w/ CO_2
    - Tailorable morphologies of Calcite, Aragonite and sometimes Vaterite
  - Filtered to obtain dried cake
  - Particles dis-agglomerated and sized by grinding
  - Stearic acid treatment



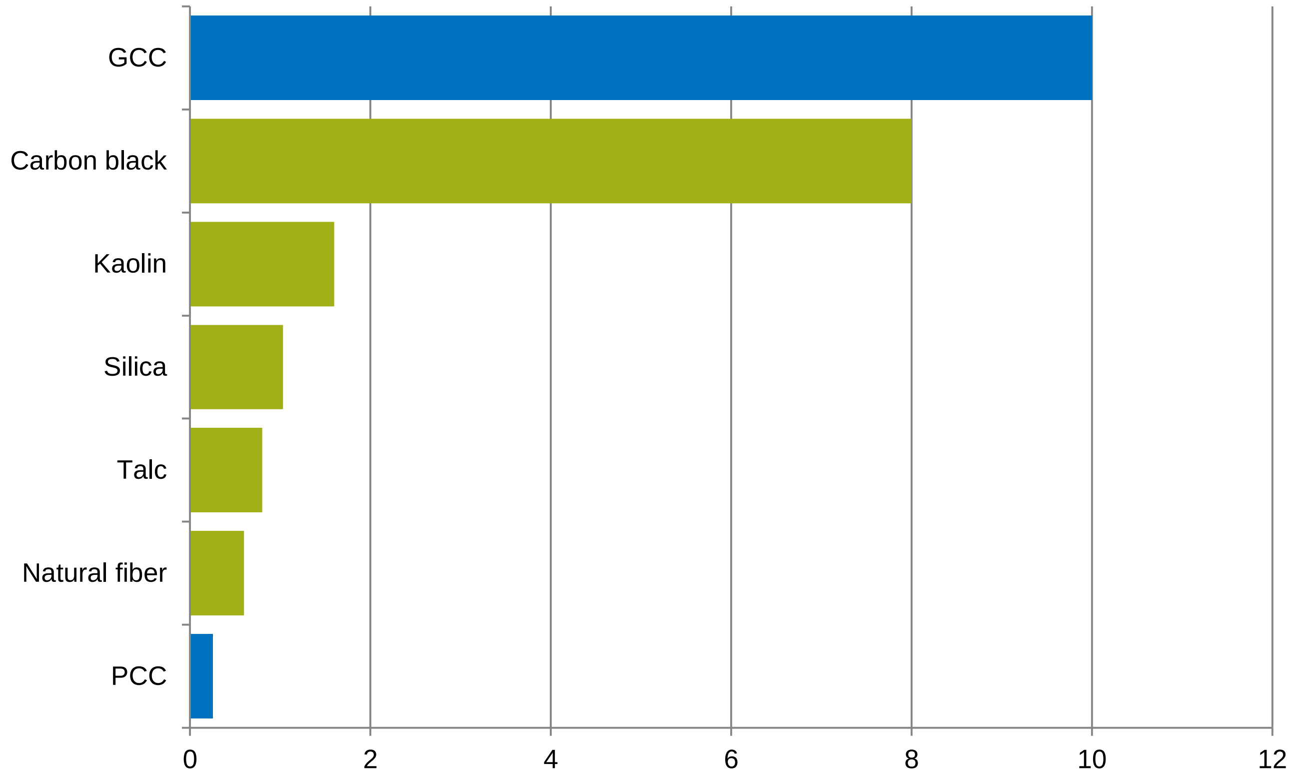
PCC was first produced in 1841 by John Sturge Ltd. In England

Ground vs. Precipitated Calcium Carbonate

Ground Calcium Carbonate (GCC)	Precipitated Calcium Carbonate (PCC)
• Morphology – Rhombohedral • Dry ground – Down to 20 microns • Wet ground – 3-12 micron median dia. (45 micron top cut) – Ultrafine 0.7-2.0 micron dia. (10 micron top cut) • Stearate treatment	• Morphology – Aragonitic (clustered) – Scalenohedral – Spherical (vaterite) • Small particle size – Fine 0.7 micron median dia. – Ultrafine 0.07 micron median dia. • High brightness • Stearate treatment

Global Production GCC vs. PCC

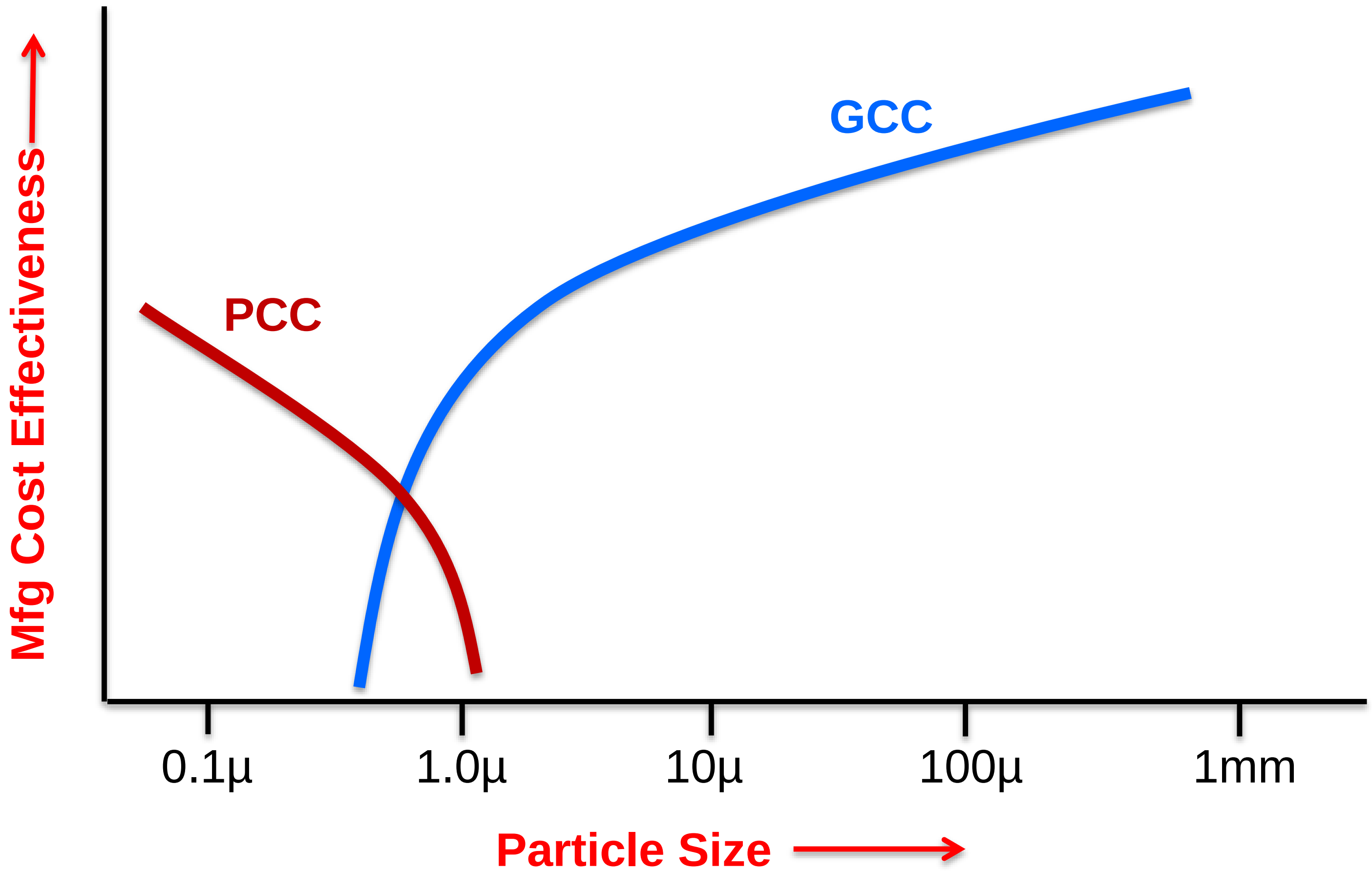
Metric Tons per year x10^{6}



Source: (AMI 2007+Imerys)

Ground vs. Precipitated Calcium Carbonate

Comparison of Production Cost Effectiveness



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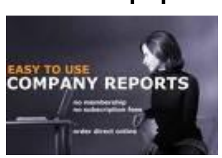
Part II

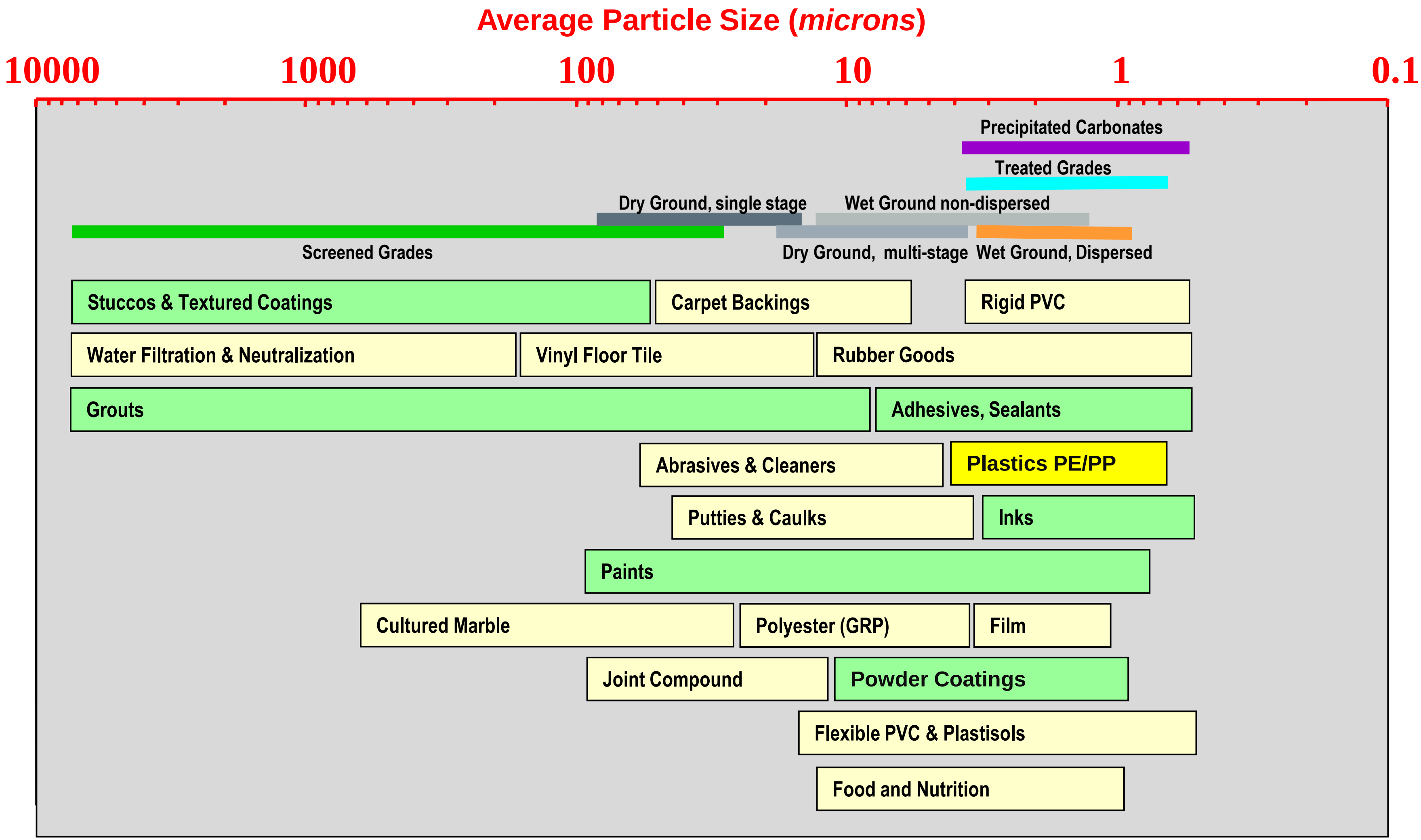
Applications and Physical Properties of Calcium Carbonate

Industrial Applications for $CaCO_3$

MARKET	APPLICATION				
Consumer Goods & Packaging	Breathable Film 	Fibers & Nonwovens 	Packaging 		
Paint and Coatings	Deco 	Inks 	Automotive 	Marine 	
Building & Construction	Adhesives 	Sealants 	Cement & Mortars 	Roofing 	PVC 
Food, Pharma & Personal Care	Cosmetics 	Toothpaste 	Pharma 		
Paper	Office paper 	Packaging 	Magazines 	Specialty 	

Source: Imerys

Key Applications by Particle Size



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Source: Imerys

Calcium Carbonate in Plastics

Applications

- Blown film
- Thermoformed sheet
- Injection molding
- Blow molding
- Film extrusion
- Raffia (slit tape)

Key benefits

- Quality
  - Improving toughness
- Opacity/Whiteness
  - use as a TiO_2 substitute
- Productivity
  - Increased speed
- Economy
  - Filler

Designing with Mineral Products

Managing and applying mineral characteristics…

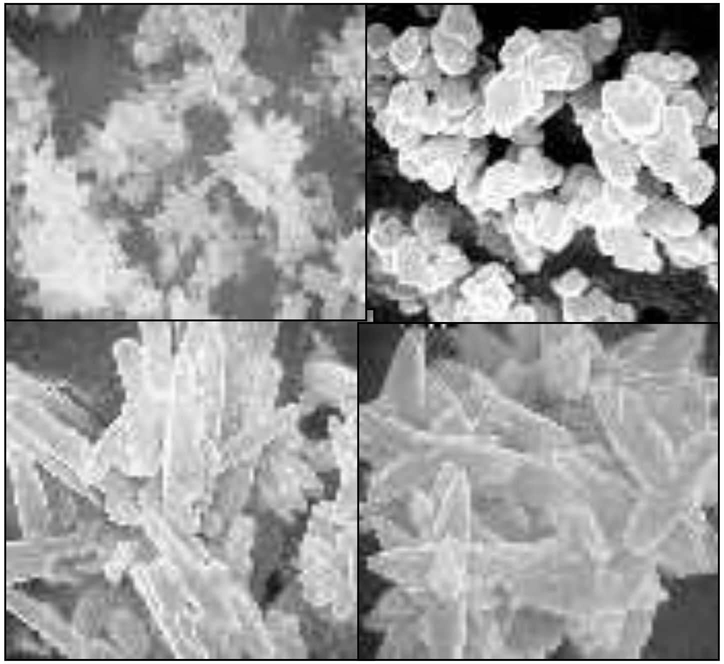
- Particle size
- Particle shape
- Particle packing
- Crystal microstructure
- Color
- Refractive index
- Specific gravity
- Hardness
- Chemical composition
- Surface character

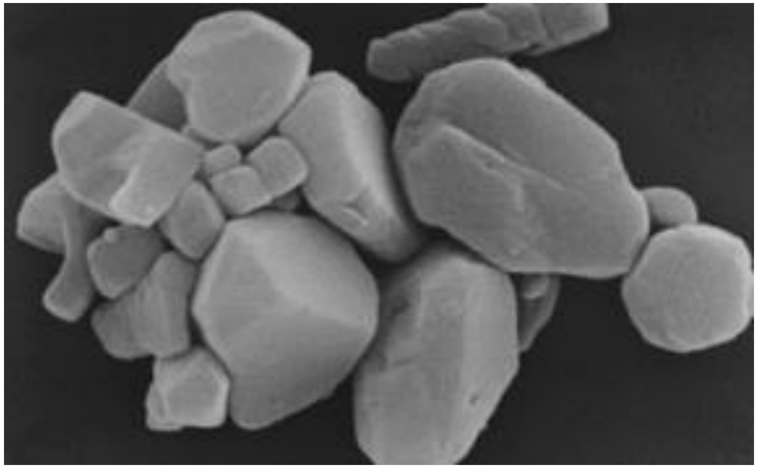
…to deliver enhanced performance in end use

- Opacity
- Density modification
- Wear / abrasion resistance
- Barrier properties
- Bonding
- Mechanical reinforcing
- Processing advantages
- Chemical delivery / reaction
- Cost reduction

Basic Properties of Calcium Carbonate

Property	Specific Gravity	Whiteness	pH	Particle shape	Mohs Hardness	Inert-ness	Max. operating Temp
$CaCO_3$	*2.7*	*~ 85 - 95*	*9-10*	*Blocky*	*3*		*500°*





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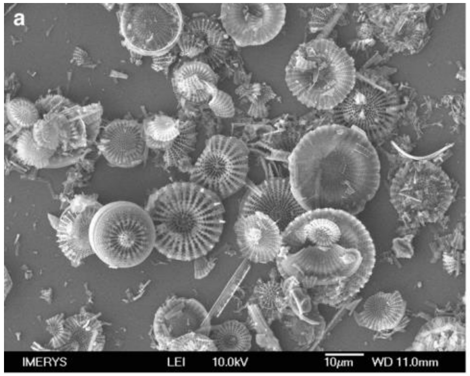
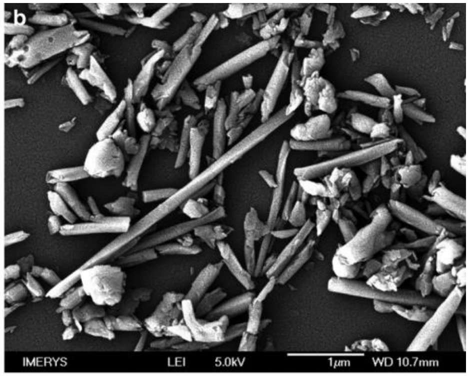
Source: Imerys

Particle Shape

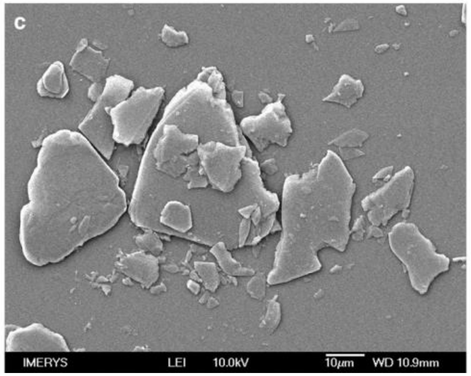
Not all particles are the same shape!

- Aspect Ratio
  - AR= Length/ Diameter
    - Spherical
    - Platy
    - Acicular





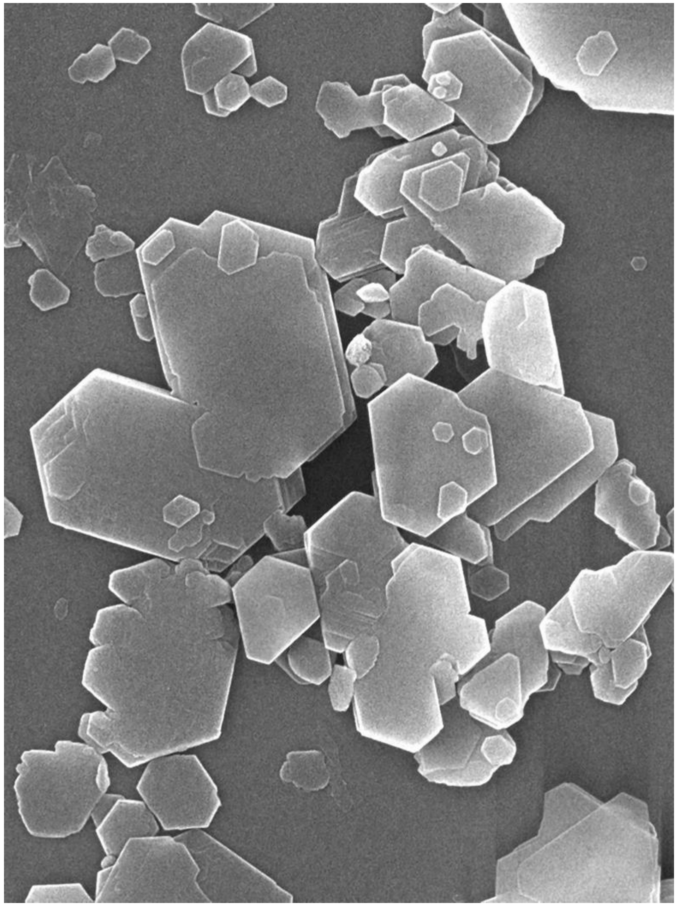
Note that most measuring techniques report size as **ESD** (Equivalent Spherical Diameter)



Particle Size Distribution (PSD)

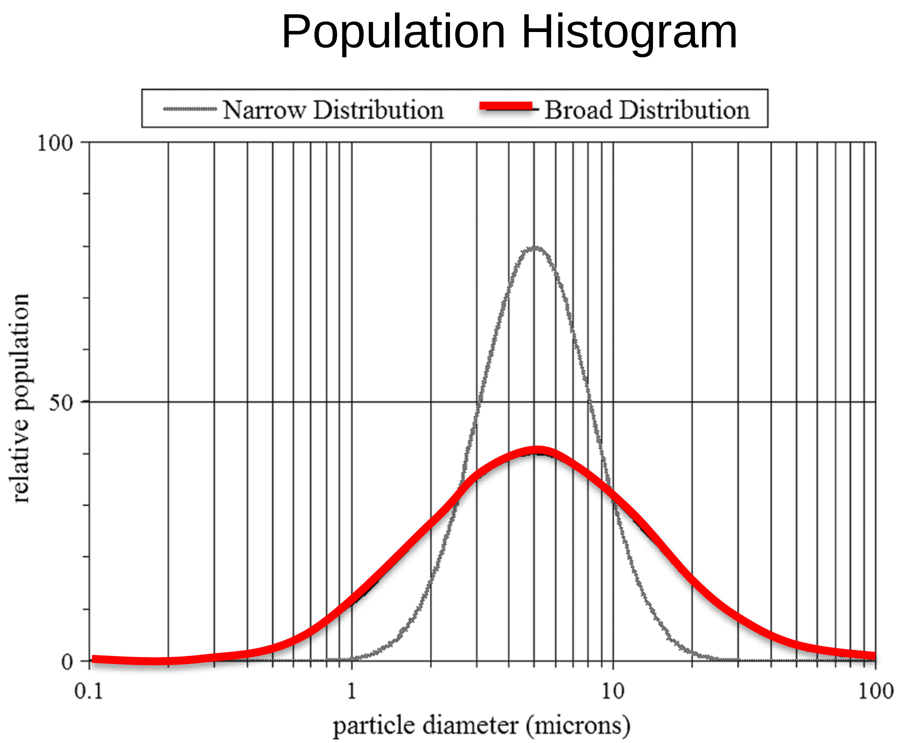
How is particle size defined?

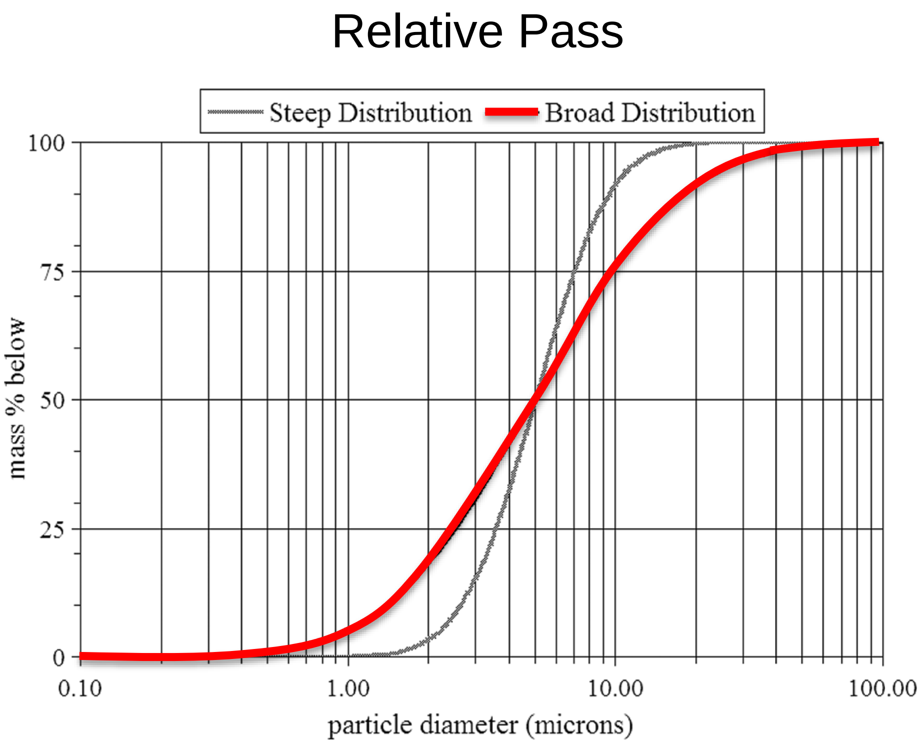
- Not all particles are the same size!
- **Particle Size Distribution,** or PSD, is the preferred method of describing the quantity or percent of particles that are at (or under) a stated size



Particle Size Distribution (PSD)

- Two graphical methods for distribution by size
- Log scale for particle diameter (X-axis)





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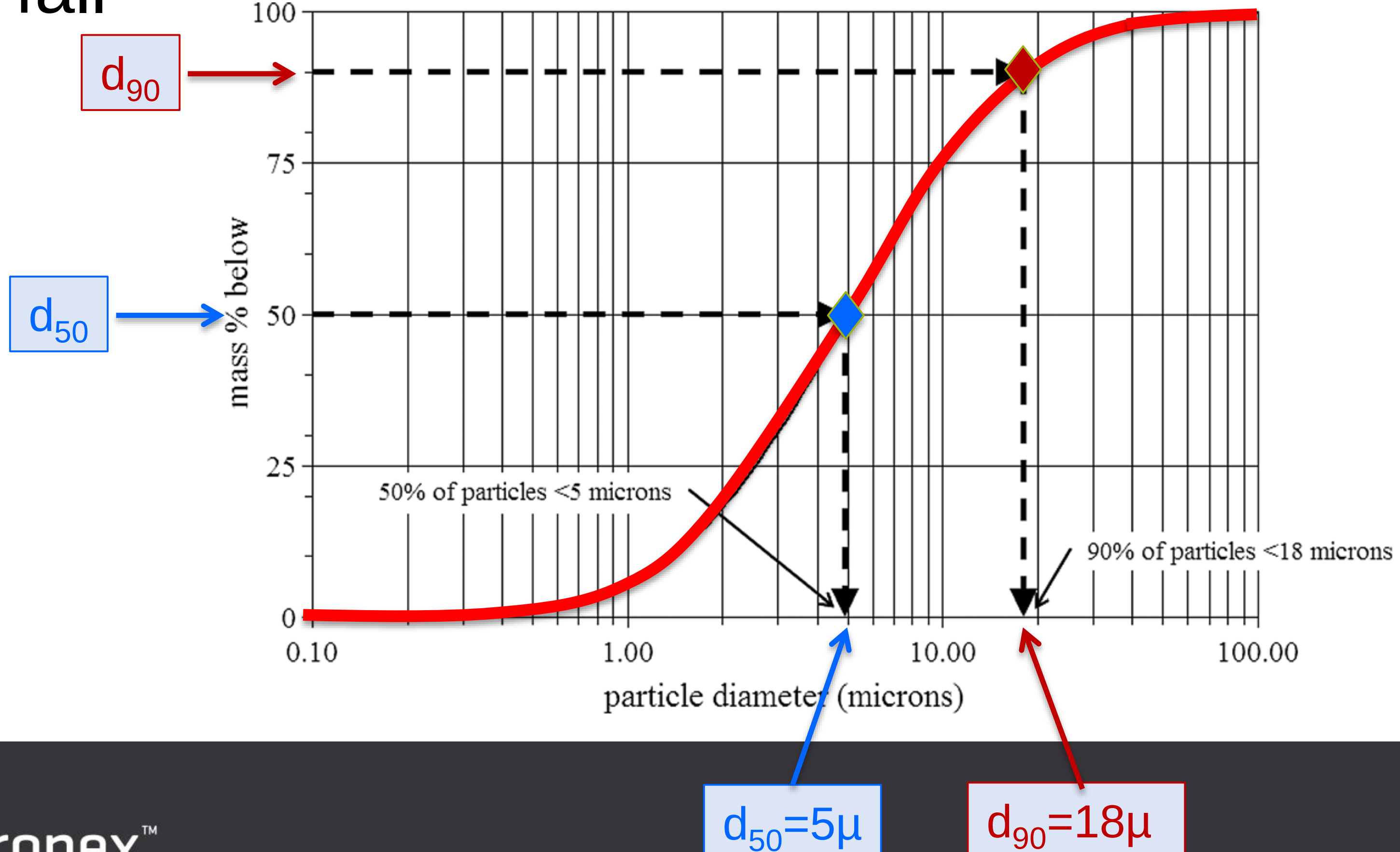
Understanding the PSD Chart

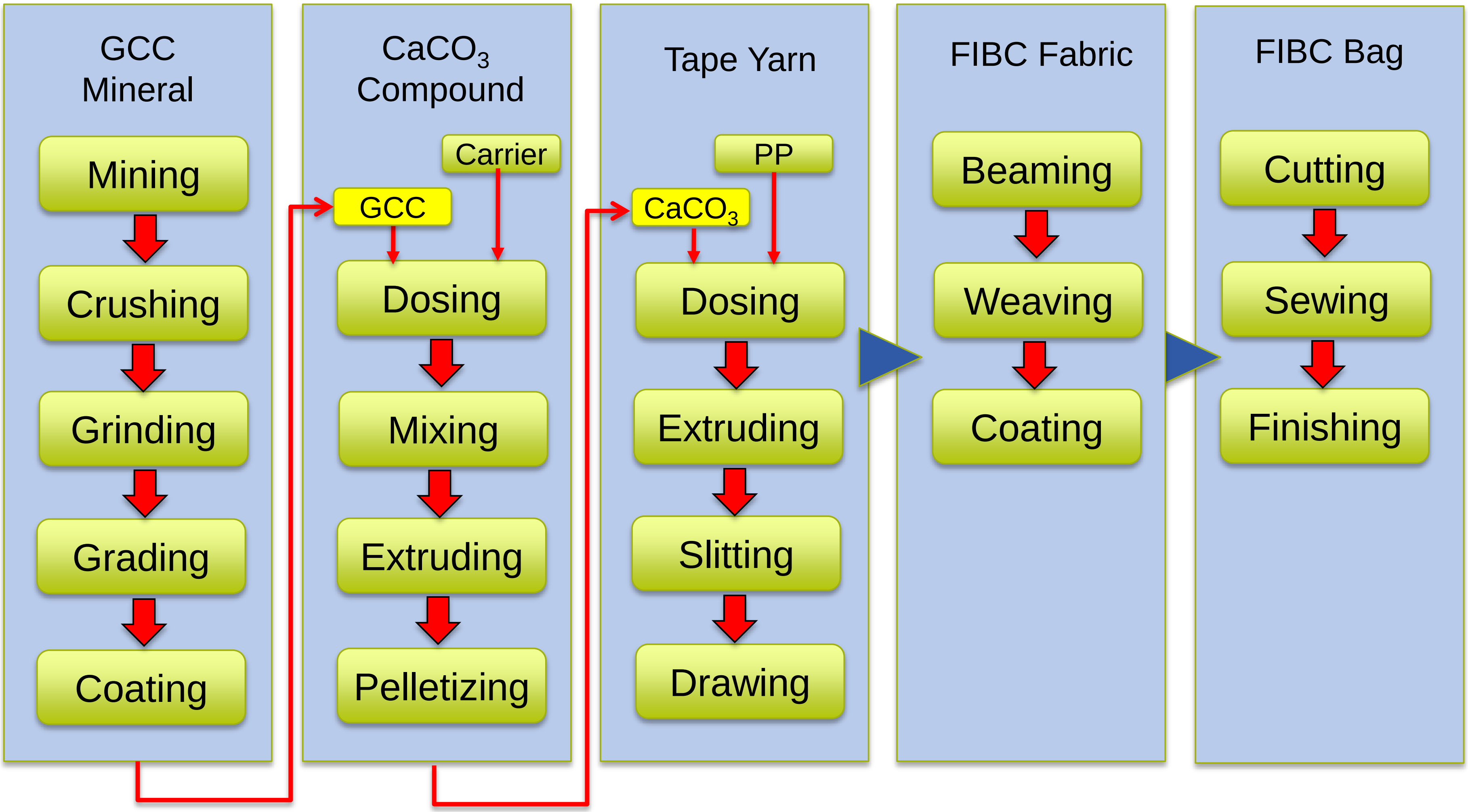
- d_{50} or Mean= size below which 50% particles fall
- d_{90} or Top Cut= size below which 90% particles fall



Part III

Calcium Carbonate in FIBCs

Process Flow of $CaCO_3$ in FIBC



CaCO3 Concentrate- Typical Data Sheet

Mineral Specification

- Mineral Type:
  - Calcium Carbonate
- Density
  - 2.71 g/cc
- Particle Size:
  - Mean (d$_{50}$)= 1.5 microns
  - Top Cut (d$_{95}$)= 10 microns
- Coating
  - Stearic acid

Compound Specification

- Carrier Resin
  - Type: LLDPE
  - Density: 0.916 g/cc
  - Melt Flow: 20 g/10 min
- Loading
  - 50% by weight
- Pellet Count
  - 38 pellets/g
- Net Pellet Density
  - 1.81 g/cc
- Net Melt Flow
  - 10 g/10min
- Heat Stability
  - 520 ºF

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Calcium Carbonate Product Portfolio

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Imerys Product	Comment	Average Size (u)	Top Size (u)	Coated	Grinding Process
FL201S	*Top of the line product for thin films, non-woven fibers (high TS)*	1.5	10	Y	Wet
Supermite	*Uncoated version of Supercoat*	1.5	10	N	Wet
Supercoat	*Coated version of Supermite*	1.5	10	Y	Wet
Atomite	*Larger particle size/top cut (3/15)*	3	15	N	Wet
Kotamite	*Coated version of Atomite*	3	15	Y	Wet
Gamaco	*Low Cost; X-mill has higher fines than dry (=more surface area)*	3	15	N	X-mill
Gamaco	*Less surface area than X-mill*	3	15	N	Dry
CalWhite	*Synthetic paper and tape; 6/20 micron particle size/top cut*	6	20	N	Dry
SFPE	*"Snowflake PE" is wet ground version of CalWhite*	6	20	N	Wet
#10 White	*Largest particle size used in plastics (10/45)*	10	45	N	Dry

Experimental Method

Sample Preparation

- 10 different $CaCO_3$
- Masterbatch at 50% PP
- 80 sample conditions (x3) at 1500 denier
- Factors
  - Particle size
  - Grind (wet/dry)
  - Coating
  - Draw ratios

Evaluation of Response

Yarn Tests Performed

- Tenacity (breaking strength/denier)
- Modulus (stiffness)
- Elongation (% stretch at failure)
- Toughness (energy absorption)

Material Characterization: Stress-Strain

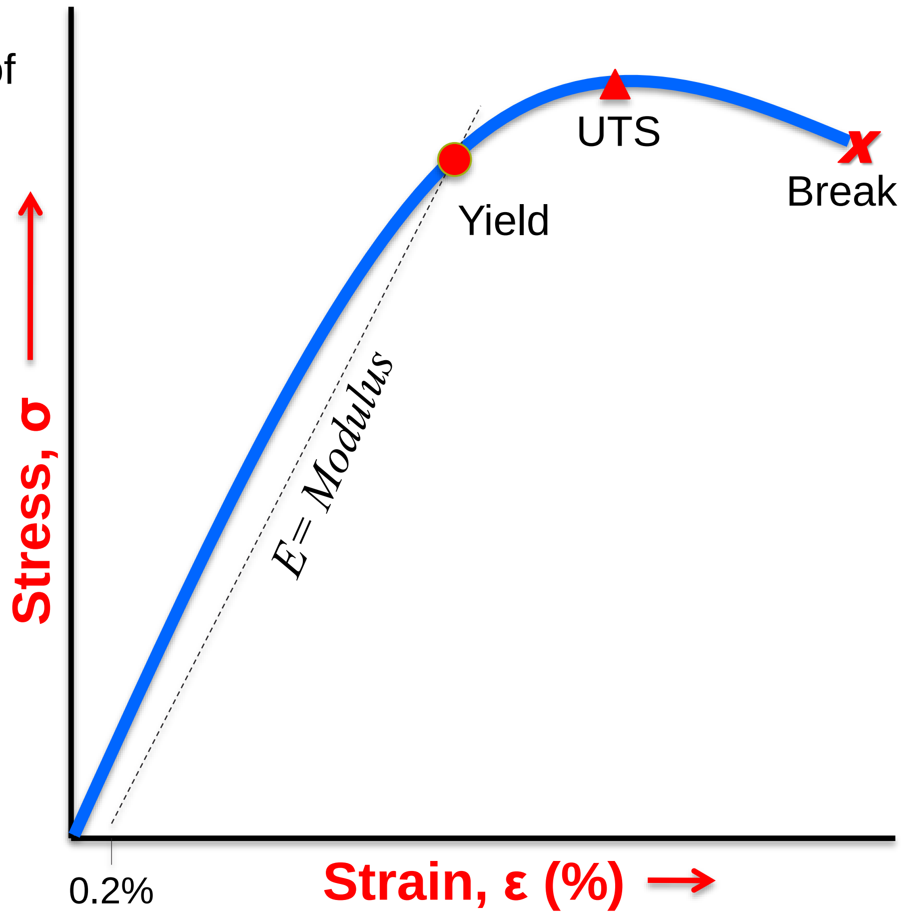
Stress (σ)
Strength or load applied to specimen
Strain (ε)
Elongation or % change in dimension of sample during tensile test
Young's Modulus (E)
The slope of the linear portion of the stress-strain curve at 0.2% deformation:

$$E=\sigma/\varepsilon$$

where σ *= strength or load applied*
ε *= strain or elongation* $(\Delta L/L_0)$

Yield Strength
Strength or load at the point material yields (deformation rate increases)
Ultimate Tensile Strength
The highest strength or load the specimen endures
Breaking Tensile Strength
The strength at which the specimen fractures (fails)

Typical stress-strain curve from testing FIBC tape yarns on a tensile tester



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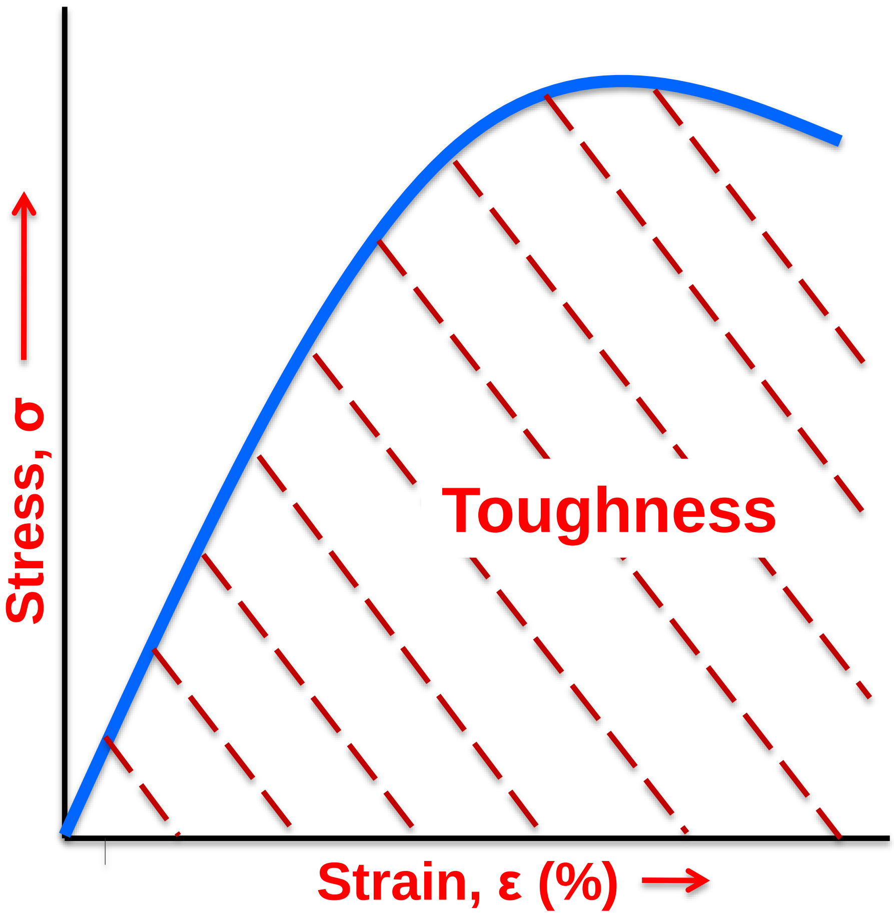
Material Characterization: Stress-Strain

Tenacity = (Breaking Strength)/(Yarn Denier)

- Because not all samples have the same denier, the breaking strength is divided by the denier so that all samples can be compared (i.e. normalized)

Toughness = Energy under the curve

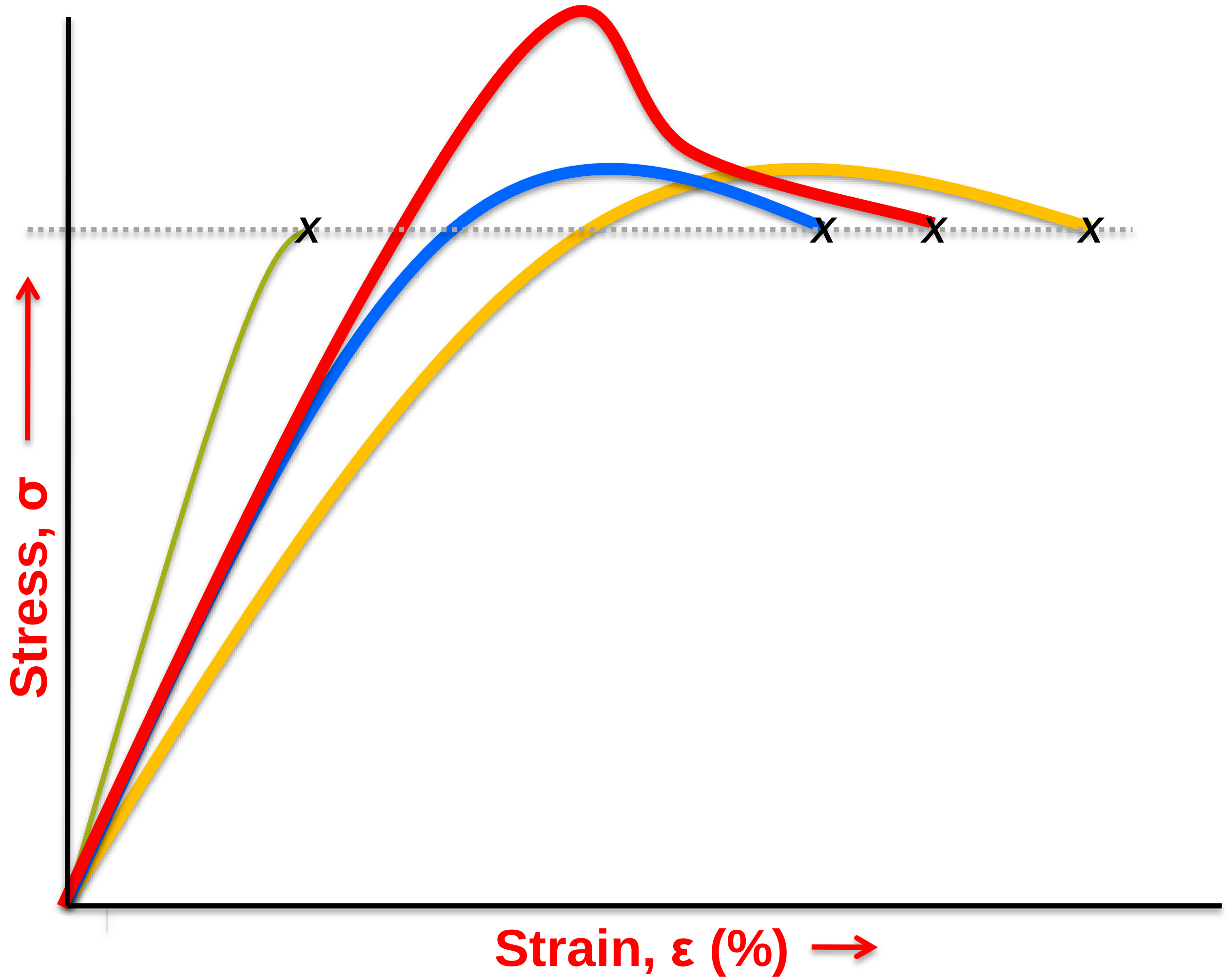
- The area under the stress strain curve
- The inverse of toughness is brittleness



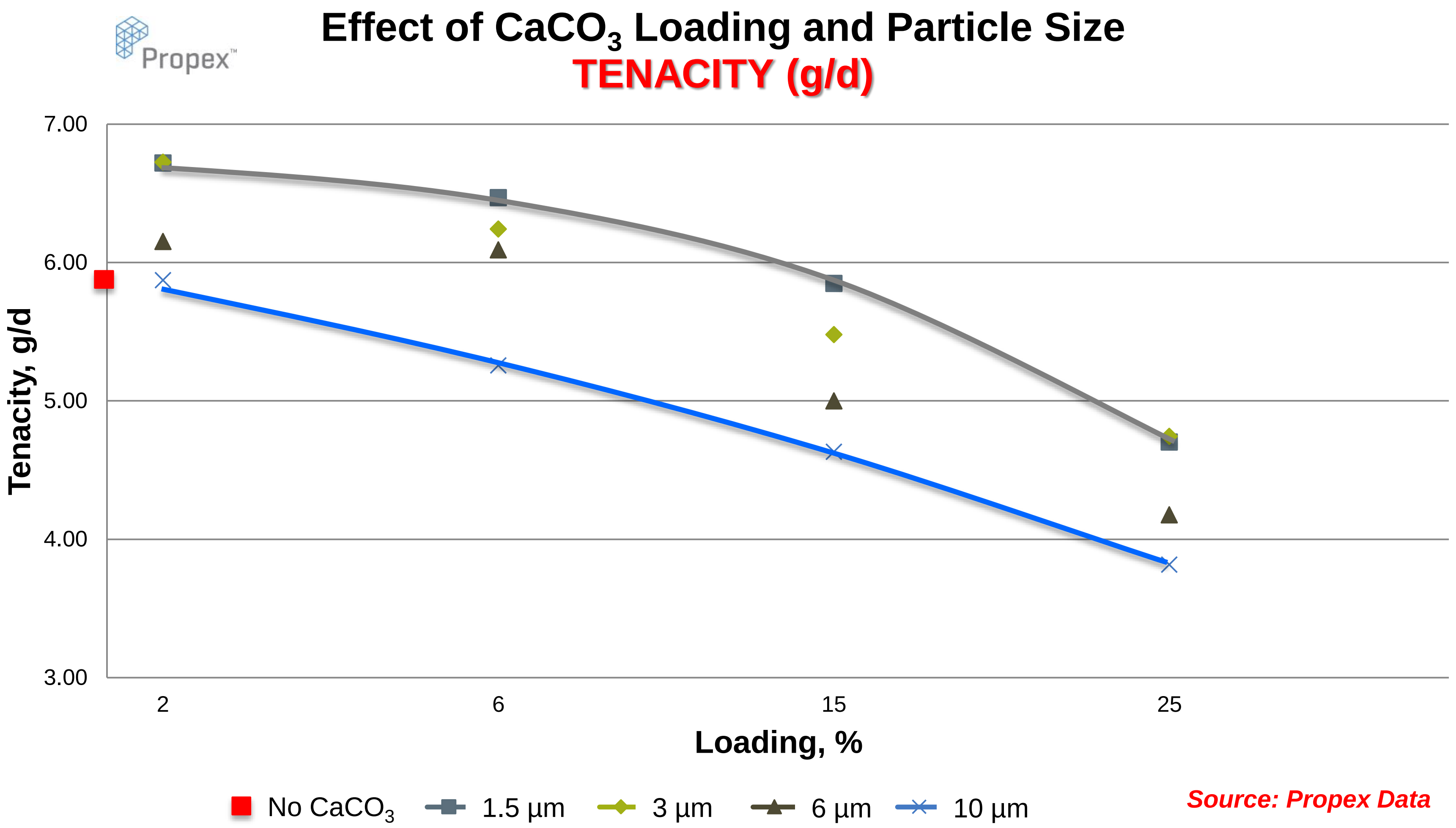
Comparison of Stress-Strain Behaviors

All four materials have the same breaking strength!

…yet all have quite different modulus and toughness



Effect of $CaCO_3$ in PP Tape Yarns



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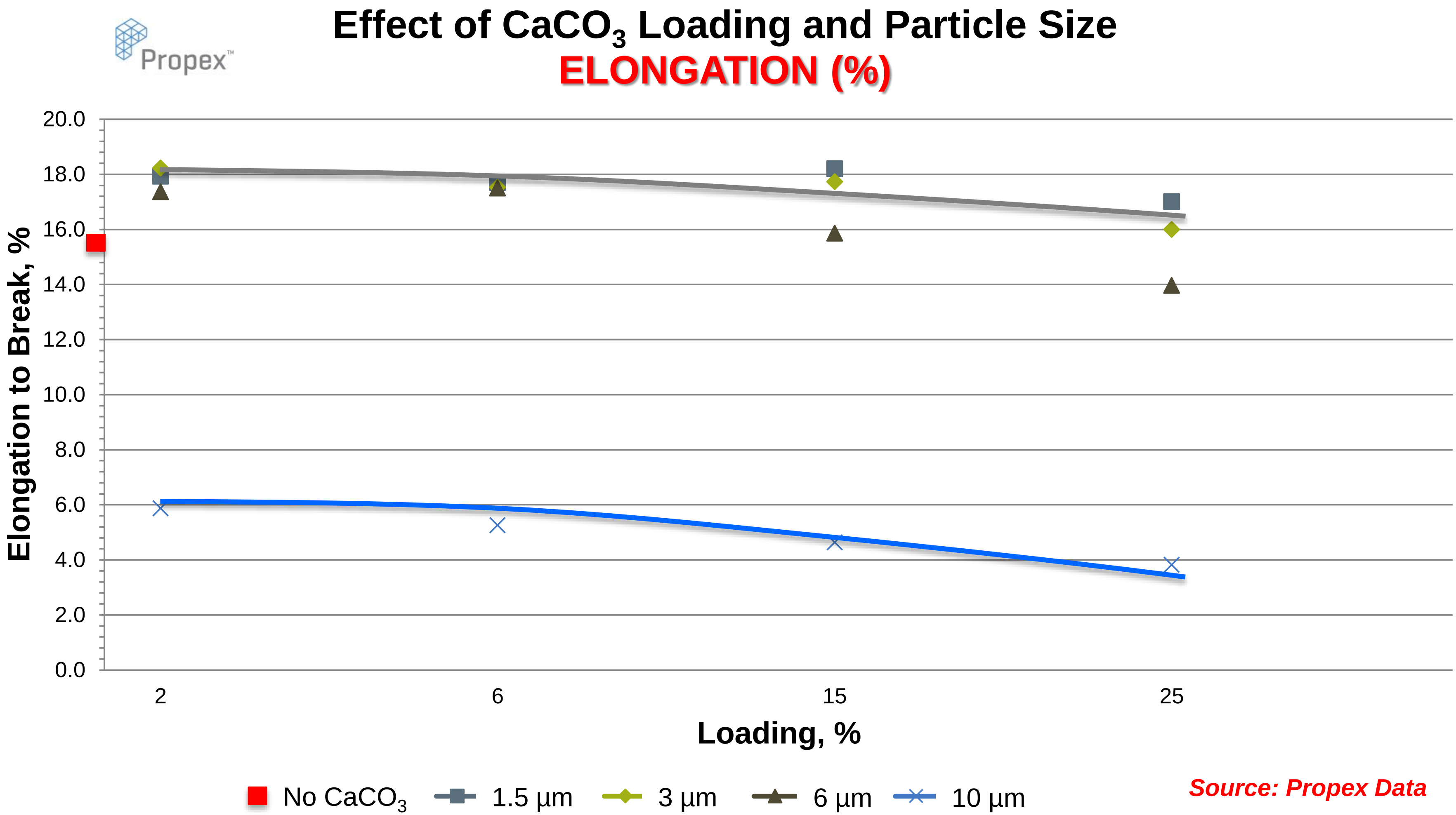

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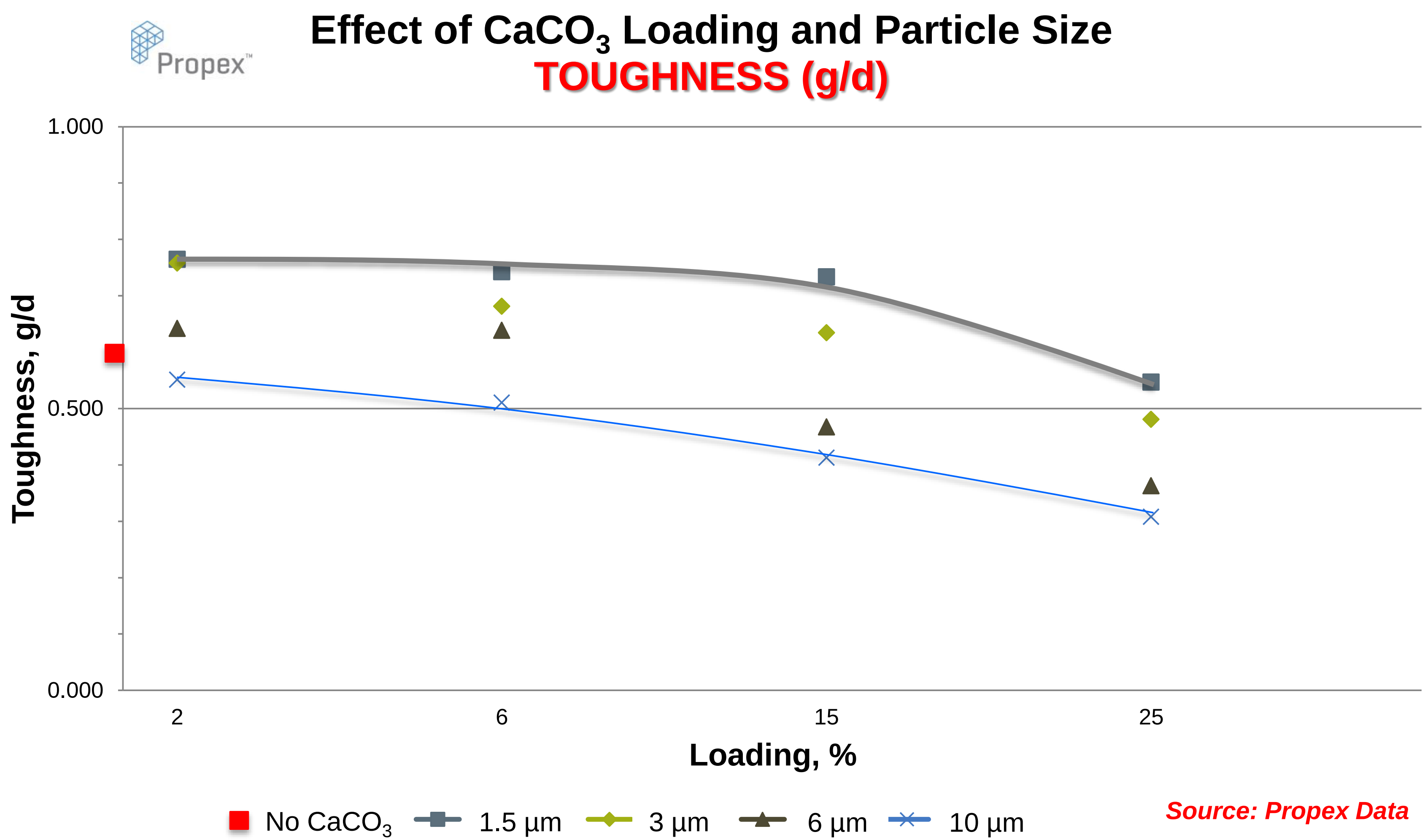
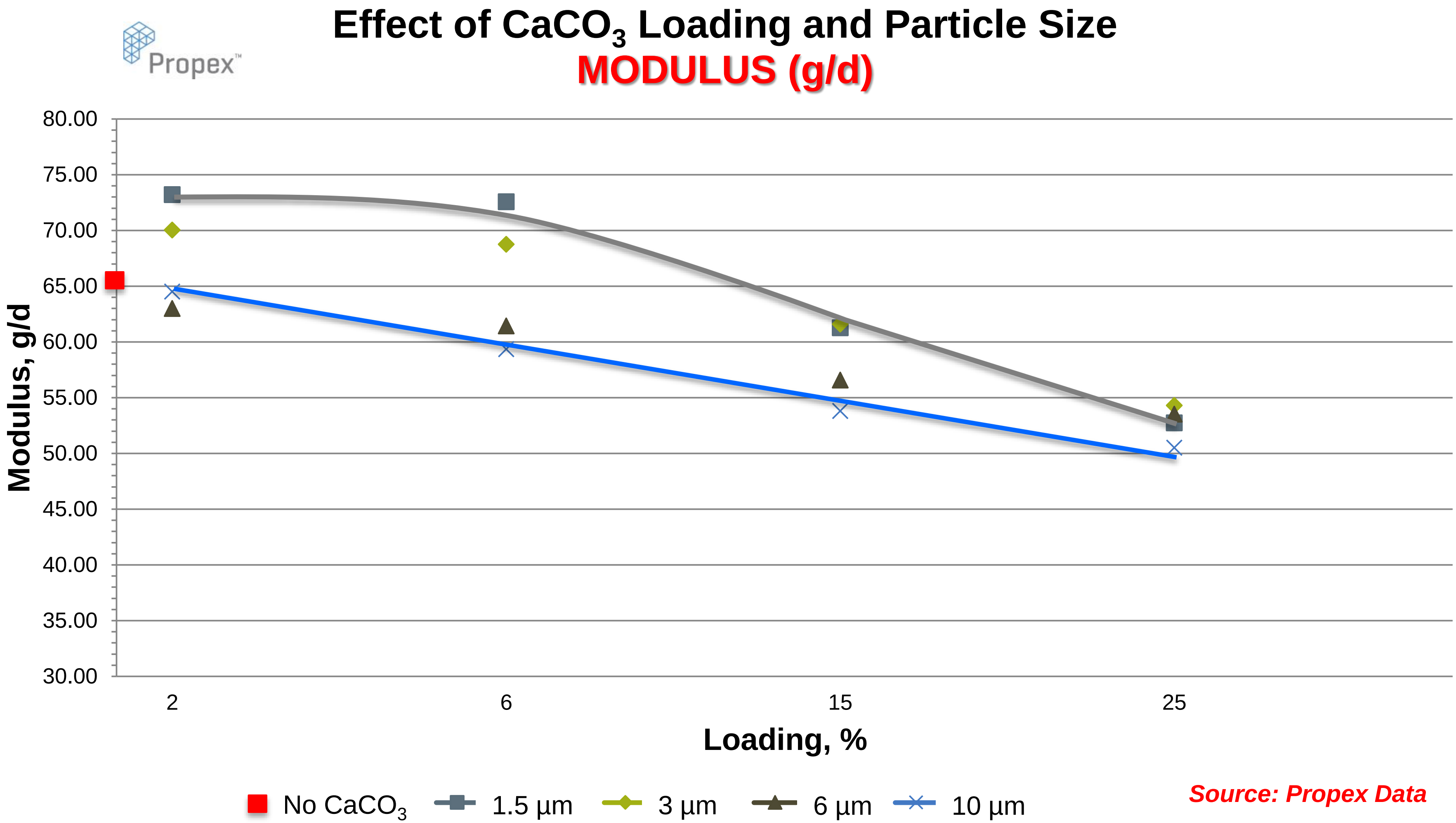


Source: Propex Data

Effect of $CaCO_3$ in PP Tape Yarns



Source: Propex Data

CTQ Elements for $CaCO_3$ in FIBC

Critical-to-Quality

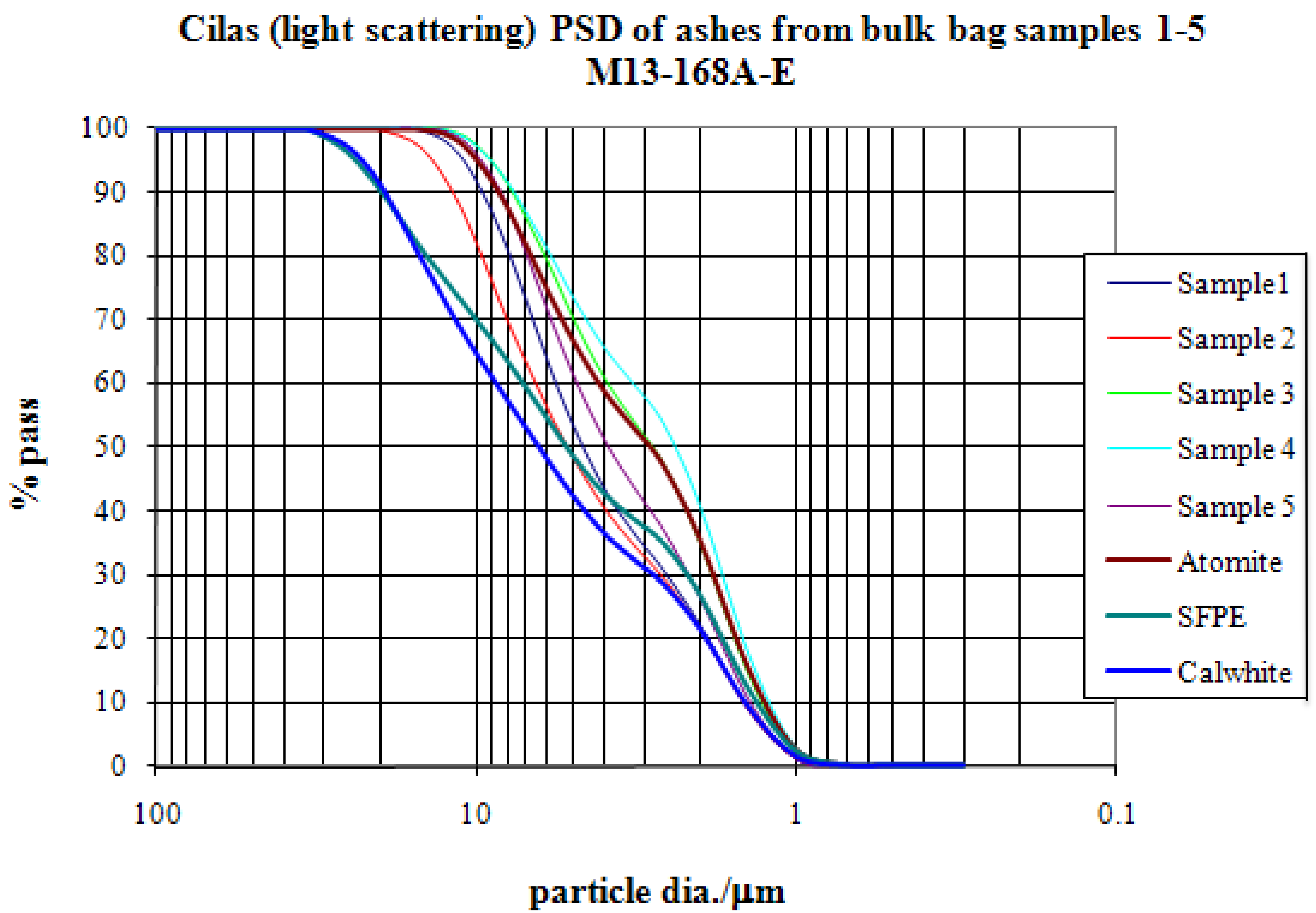
- Particle Size
- Surface Treatment
- Dispersion and distribution
- Loading

CTQ Elements for $CaCO_3$ in FIBC

Critical-to-Quality

- Particle size
  - Large particle size is not suitable for producing the thin, highly drawn PP tapes used in FIBC
  - Best performance gains in tenacity and toughness are obtained using GCC calcium carbonate of smaller particle size, e.g. 1-3 micron

Particle Size Distribution (PSD)



CTQ Elements for $CaCO_3$ in FIBC

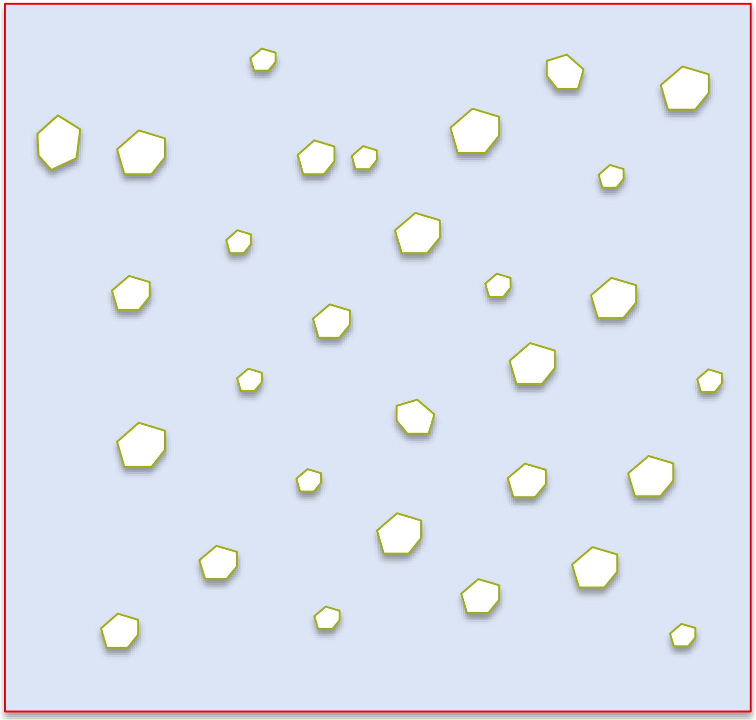
Critical-to-Quality

- Surface treatment (particle coating)
  - Stearic acid coating modifies surface tension for better adhesion to carrier and/or matrix
  - Prevents agglomeration of finer particles and hence improves **dispersion**

CTQ Elements for $CaCO_3$ in FIBC

Critical-to-Quality

- Dispersion
  - Dispersive Mixing is the ***reduction of the size*** of cohesive minor components
- Distribution
  - Distributive Mixing is the ***uniform spatial spreading*** of the minor components



Source: "Analysis of Mixing in Polymer Processing Equipment", Ica Manas-Zloczower

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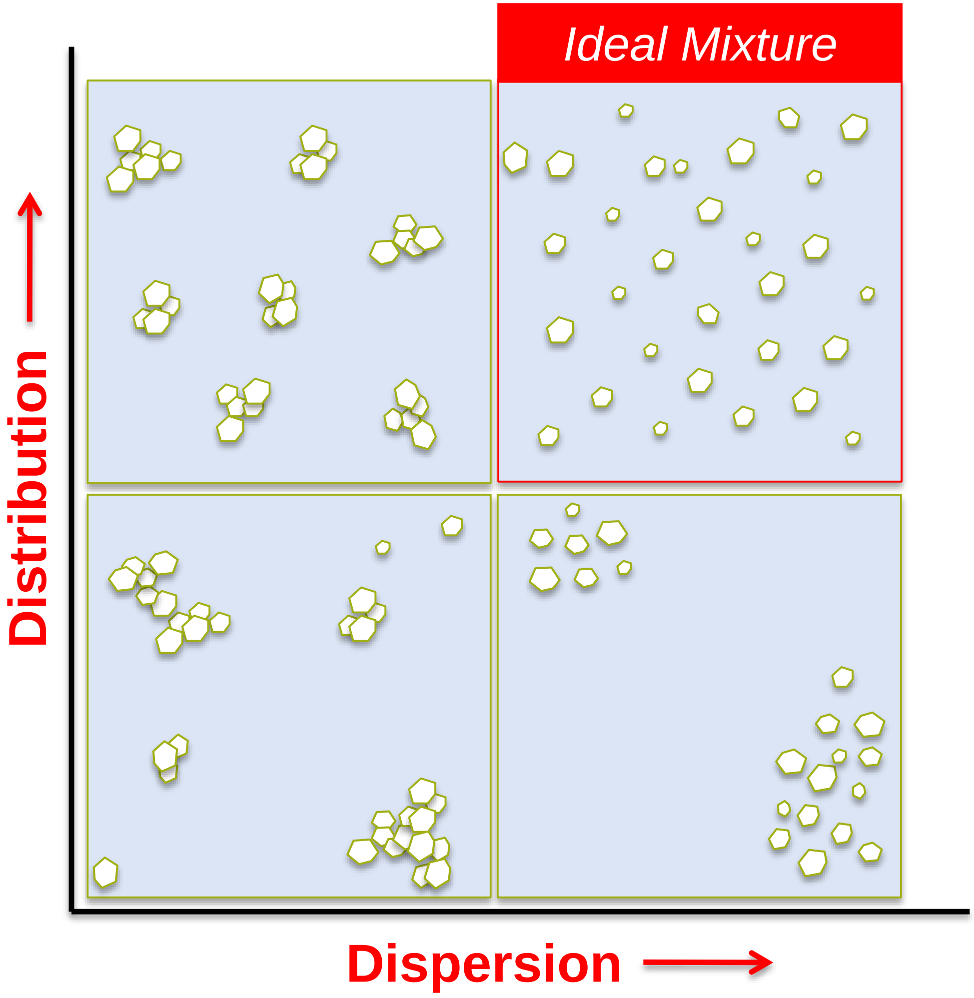

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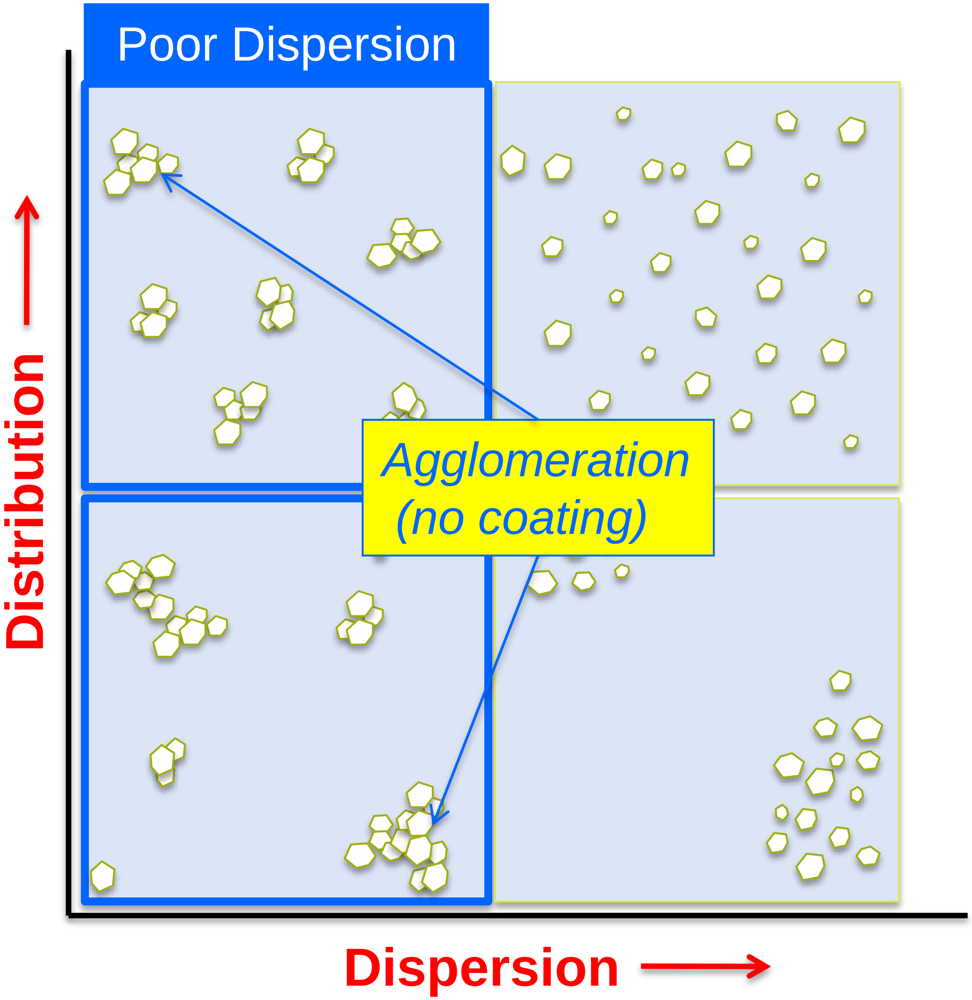

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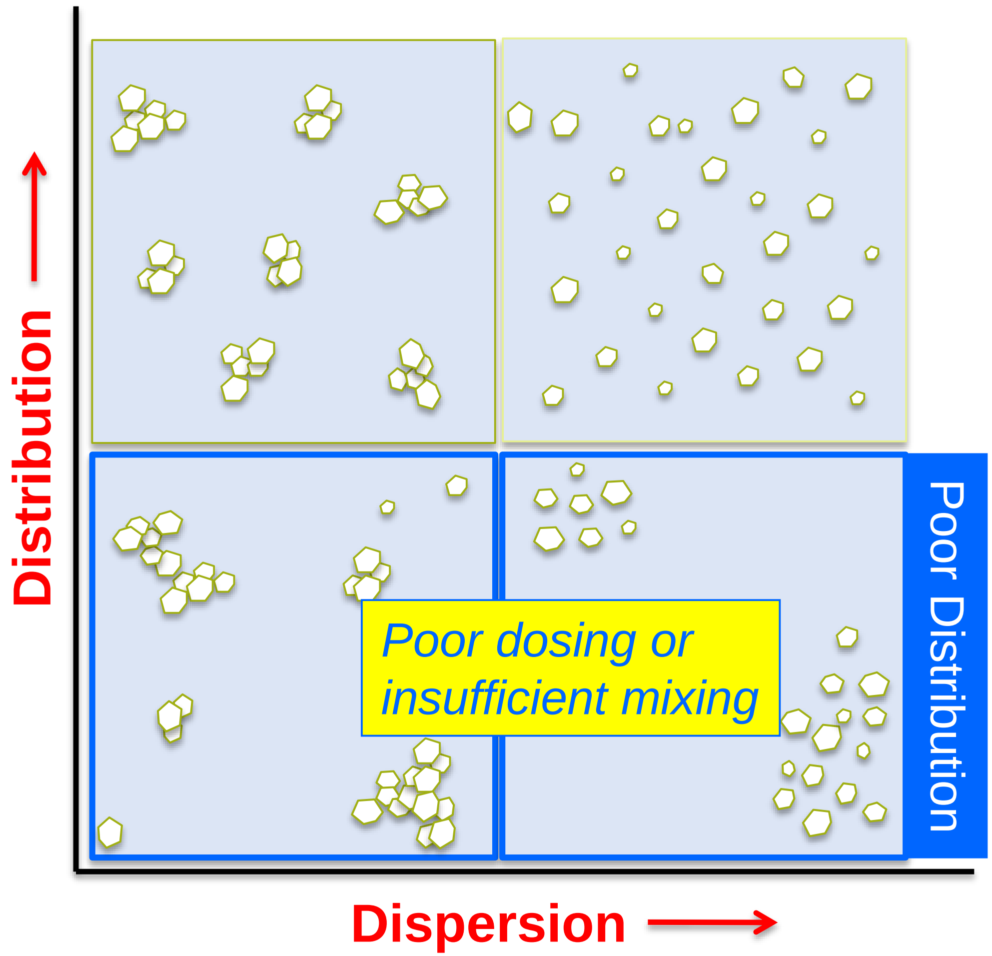

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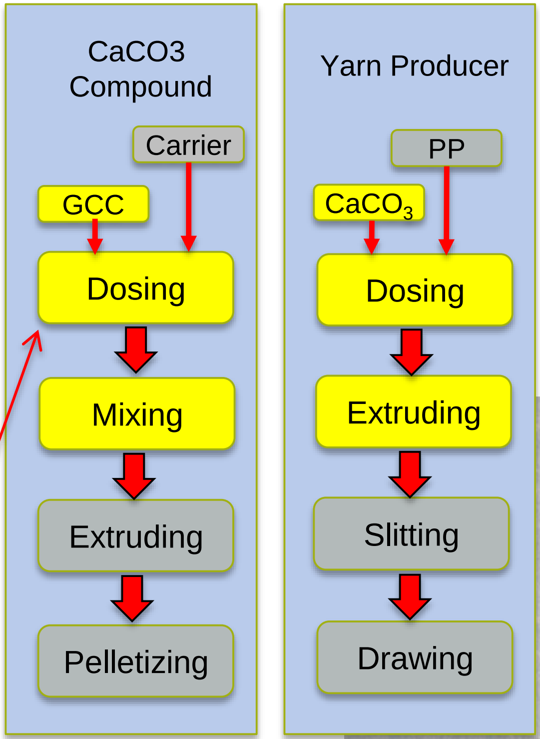
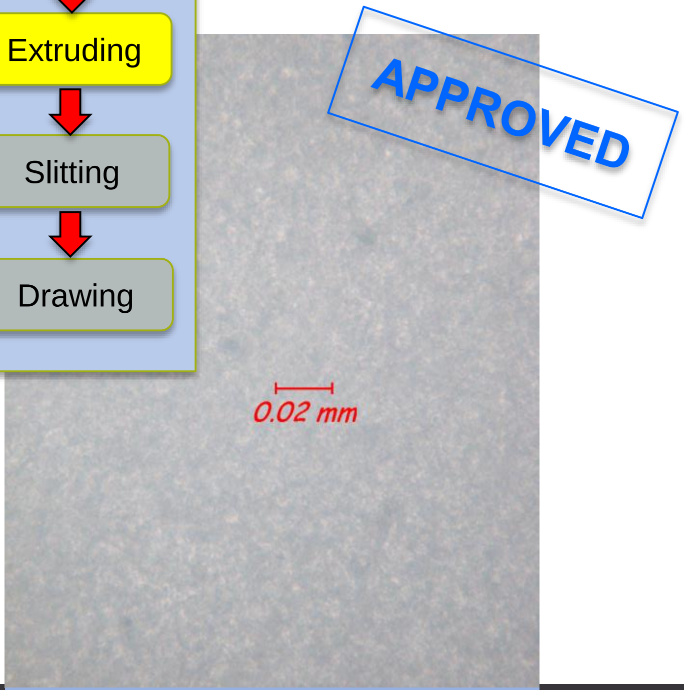
Source: *"Analysis of Mixing in Polymer Processing Equipment", Ica Manas-Zloczower*

CTQ Elements for $CaCO_3$ in FIBC

- Dispersion and Distribution
  - Good dispersive and distributive mixing requires carefully controlled process conditions in the compounding and tape extrusion stages



Mixing problems or flaws that occur during the compounding stage cannot be corrected during yarn extrusion



1.5 micron $CaCO_3$

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CTQ Elements for $CaCO_3$ in FIBC

Critical-to-Quality

- Loading *(aka Let Down Ratio or LDR)*
  - Best performance gains in tenacity and toughness are obtained at modest mineral loadings
  - High loading: raw material savings (PP) comes at the expense of yarn/FIBC performance

Why use Calcium Carbonate in FIBC's?

Motivations for using Calcium Carbonate in FIBC fall into 3 distinct categories:

- Improving mechanical properties of the tape yarn
- Improving processing capability in extrusion
- Cost reduction through dematerialization of PP

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Performance-Grade FIBC

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Economy-Grade FIBC

Why use Calcium Carbonate in FIBC's?

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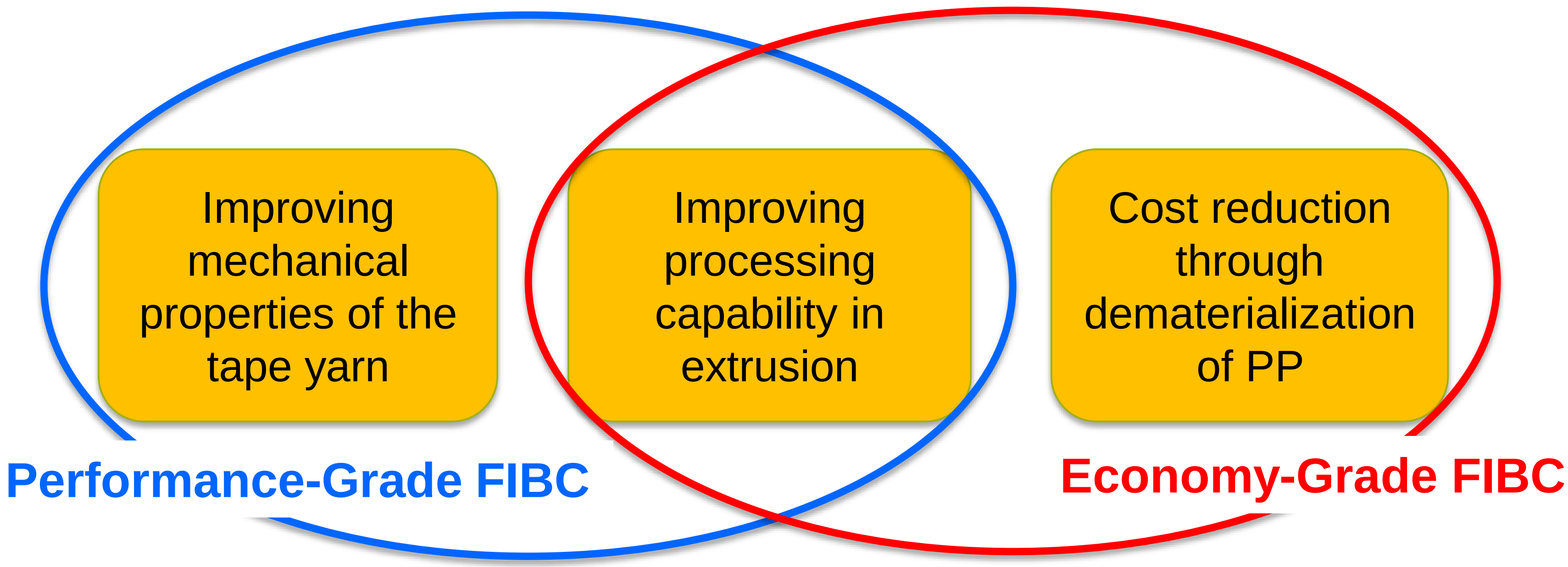

Why use Calcium Carbonate in FIBC's?

Benefits of $CaCO_3$ to Standard Grade FIBC Fabrics

- Mechanical Properties
  - Improves tenacity (higher drawing capability)
  - Improves toughness
  - Improves stiffness (modulus)
  - Provides opacity and whiteness
- Extrusion Processing
  - Improves extrusion efficiency
  - Reduces splitting and fibrillation of tape yarns

Risks in Improper Use of $CaCO_3$ in FIBC

- **Too large particle size**
  - Abrasive to extrusion, weaving and sewing equipment
  - Poor mechanical properties (e.g. strength, toughness)
  - Potential contamination risk to food grade materials
- **Excessive loading**
  - Poor properties (less strength at more fabric wt.)
  - Poor wear resistance to abrasion
  - Tendency of bag to release "dust" in use
- **Poor compounding and dosing**
  - High CV in mechanical properties (inconsistent)

Performance Comparison

Hypothetical Comparison

170 GSM Economy Grade FIBC woven material

- 170 g/m^2 (5.0 oz/yd^2) Uncoated
- $CaCO_3$ content= 15% by Wt.
- Mineral grade: Coarse
  - Mean particle size (d_{50})= 10 microns
  - Top cut part. size (d_{95})= 45 microns
- Effective PP= 145 g/m^2 (4.2 oz/yd^2)
- Nominal yarn tenacity= 4.6 g/d [1]
- Grab tensile= 692 N (156 lb) [2]

170 GSM Performance Grade FIBC woven material

- 170 g/m^2 (5.0 oz/yd^2) Uncoated
- $CaCO_3$ content= 2% by Wt.
- Mineral grade: Fine
  - Mean particle size (d_{50})= 1.5 microns
  - Top cut part. size (d_{95})= 10 microns
- Effective PP= 167 g/m^2 (4.9 oz/yd^2)
- Nominal yarn tenacity= 6.8 g/d [1]
- Grab tensile= 1,023 N (230 lb) [2]

At similar fabric weights the Economy Grade material is 32% lower in strength than the Performance Grade

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1. From experimental data
2. Assumes equal translation of yarn strength to fabric strength

Testing for $CaCO_3$ in FIBC Materials

Testing for $CaCO_3$ in FIBC Materials

- ASTM D5630-13
  - Standard Test Method for Ash Content in Plastics
    - Decomposition of polymeric material at 600ºC
    - Mass fraction of ash weight to original sample weight

$$W\%_{CaCO3} = \frac{W_{ash}}{W_{sample}}$$

- ASTM E168
  - FTIR (Fourier Transform Infrared Spectrometry)
    - Method used on the above ash to pinpoint mineral

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Photos: Intertek

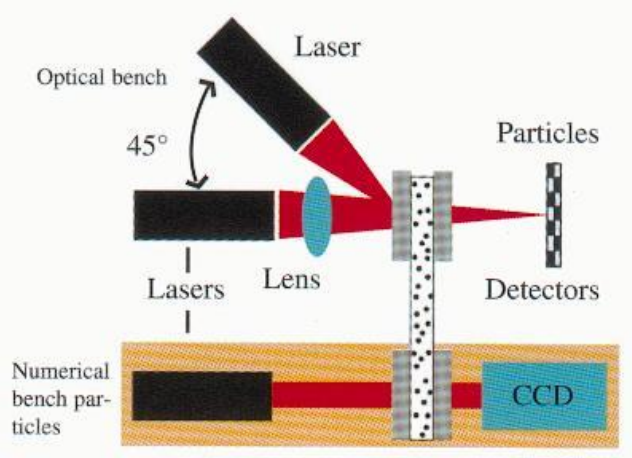
Testing for $CaCO_3$ in FIBC Materials

- Particle Size Distribution (PSD) Graphs
  - SEDIGRAPH
    - Sedimentation rate determined by X-Ray diffraction
      - Uses Stoke's Law to calculate particle size as particles settle at terminal velocity within a fluid:

$$D_p = f\,(V_t\,, \rho_p\,, \upsilon_f\,, \rho_f\,, g)$$

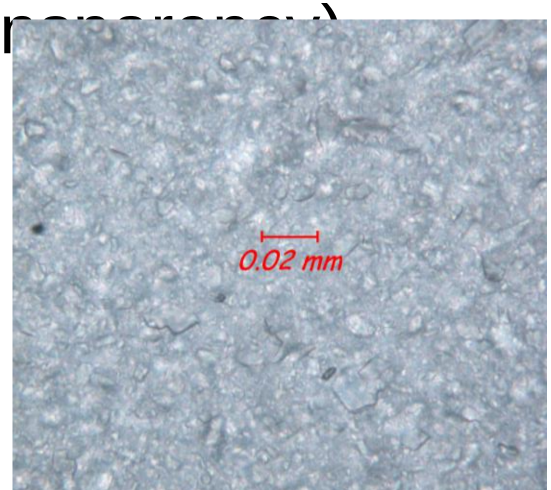
Testing for $CaCO_3$ in FIBC Materials

- Particle Size Distribution (PSD) Graphs
  - CILAS
    - Uses principle of laser light scattering to measure projected area of particle
      - Algorithm calculates the ESD (equivalent spherical diameter)
    - Practical for small sample sizes (e.g. residual from ash

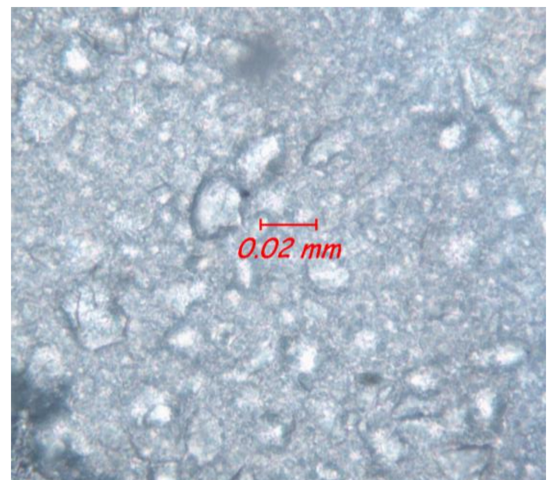


Testing for $CaCO_3$ in FIBC Materials

- Thin Film Micrography
  - Assessing particle dispersion and distribution
  - Material heated and pressed to a thin film
  - Observed at 100x to 500x magnification (tra



3 micron $CaCO_3$



10 micron $CaCO_3$

Photos: Imerys

Part IV

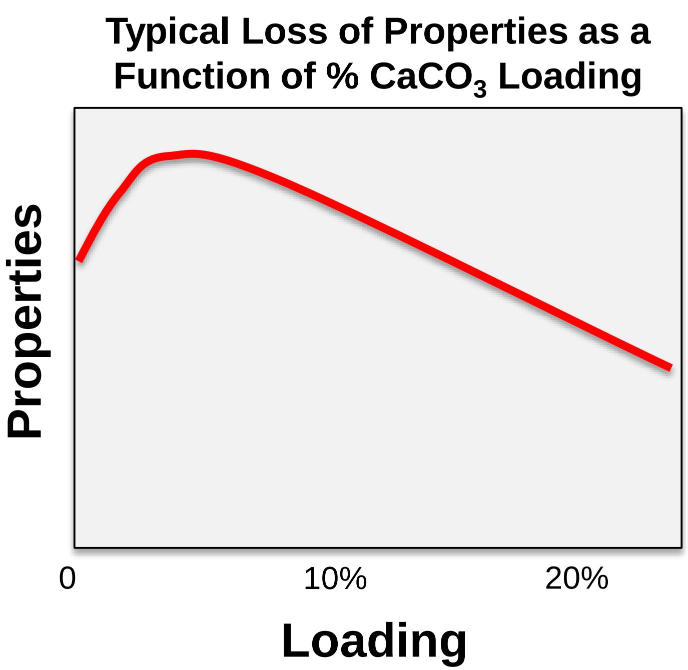
Conclusions

Summary

- Calcium carbonate content is necessary and beneficial to the manufacturing process and to the properties of PP yarns destined for FIBC.
- Control factors of performance of $CaCO_3$ in FIBC:
  - Particle size distribution
  - Surface treatment
  - Loading level
  - Mixing (proper distributive and dispersive mechanism)

Summary

- Finer particle size (<3 micron mean diameter) provide best benefit to yarn processing and yarn properties for FIBC
- FIBC's made from economy-grade fabrics that contain elevated loadings (e.g. >8% by weight) will always exhibit inferior mechanical properties (strength, elongation and toughness) regardless of mineral grade used



Conclusion

Hopefully, after today, you will now…

- **Know the sources and types of $CaCO_3$ minerals;**
- **Understand how these mineral additives are defined, measured and tested;**
- **Understand how $CaCO_3$ fits in the production of materials for FIBC's;**
- **Understand how proper use of $CaCO_3$ can improve FIBC materials…**

…and how performance can be diminished if misused .

Thank You

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