Nanoparticle Characterization Needs – From Composite Properties to Product Stewardship

The New Steel?
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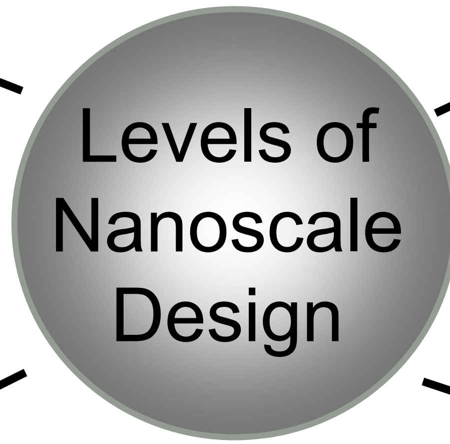
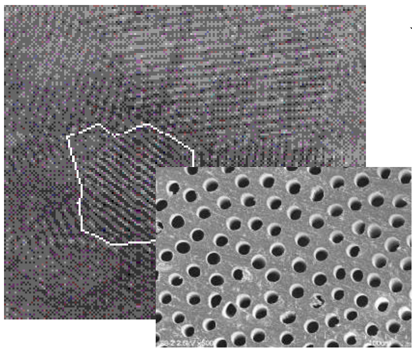
Lee Silverman
DuPont Nanocomposite Technologies
Central Research and Development
Wilmington, Delaware

The miracles of science™

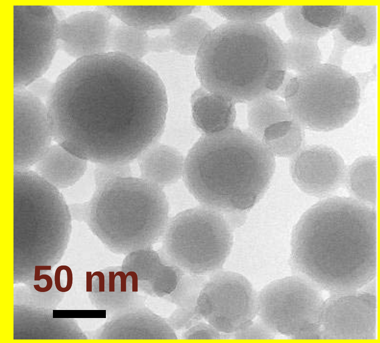
Partitioning Nanotechnology Space



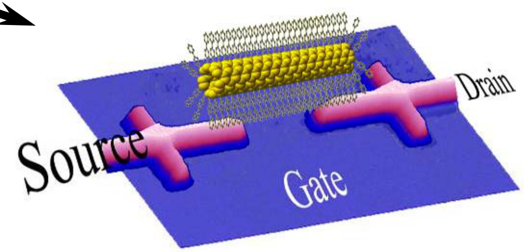
Nanostructured bulk materials
(nanoscale internal structure)

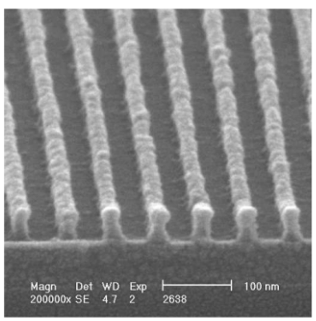


Nano Particles
(nanoscale in one or more dimensions)

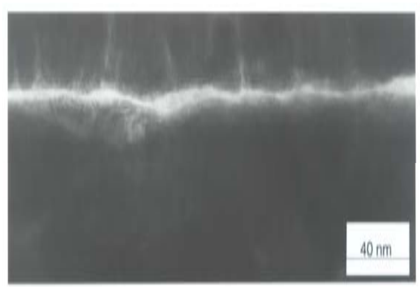


Nanodevices





Textured Surfaces:
(Physically Patterned or textured on the nanoscale)



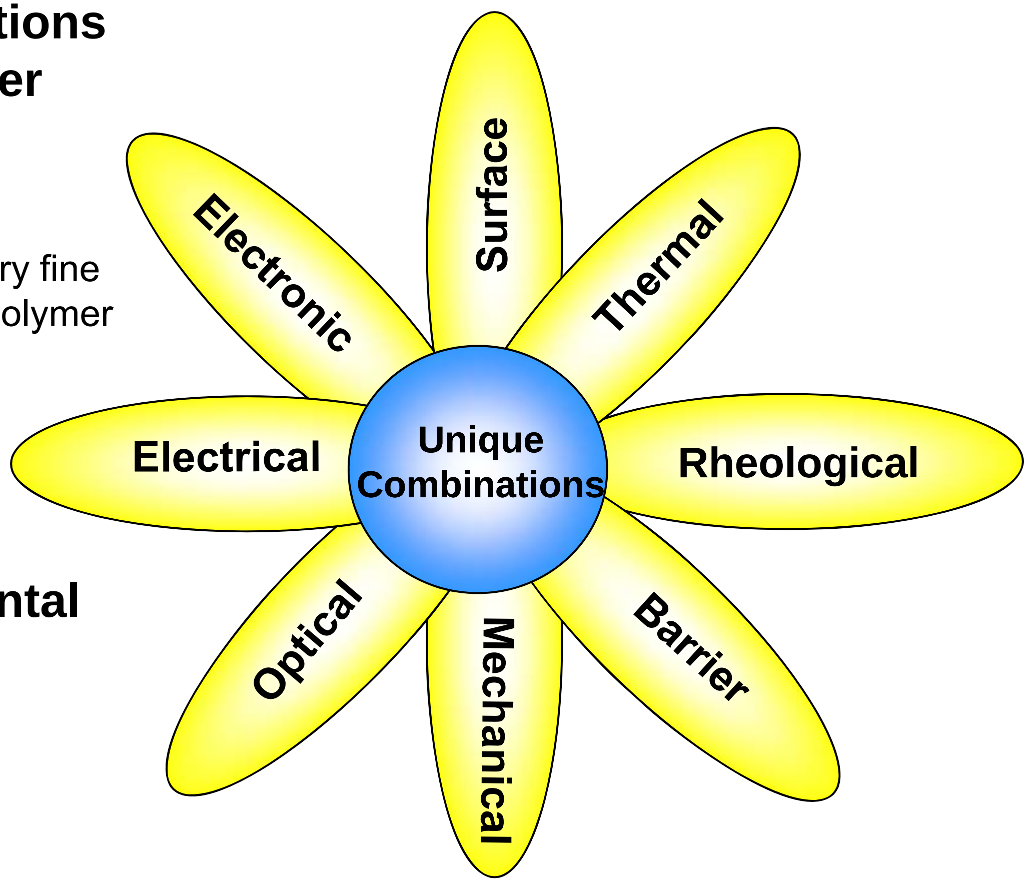
Surface Films
(Nanoscale in surface thickness only)

Nanomaterials are an Enabling Technology for Composites

Desired property combinations can be achieved with proper selection of materials and microstructure

- Manipulation of materials on very fine scale is broadly useful across polymer platforms
- Resulting materials have more function and value in use

Structure/property relationships are fundamental to material development



Nanoscale Science and Engineering and Product Stewardship:

Many nanostructures do NOT involve nanoparticles.

But most if not all nano-specific SHE questions that are being discussed relate to particles with nanoscale dimensions..

- “There is an important distinction between applications that use nanoscalar active areas on larger objects and chemicals or pharmaceuticals in which the nanometre-scale ‘active area’ is a discrete nanoparticle or nanotube …. Exposures to substances and materials other than nanoparticles are covered by existing understanding and regulation…. They are not considered further in this report except in that they may be in the form of discrete particles incorporated into materials in the nanometre size range.”

Excerpted from *Nanoscience and nanotechnologies: opportunities and uncertainties*; Royal Society and the Royal Academy of Engineering, 2004

Environmental, Health and Safety, and Product Stewardship Requires Data

"All fiber types capable of depositing in the thorax are not alike in their pathogenic potential…

A complete characterization (i.e., dimensions, fiber number, mass, and aerodynamic diameter) of the fiber aerosol and retained dose is essential."

- R. McClellan, et. al. – Regul Toxicol Pharmacol, 16 (1992) 321-64

"A robust structure/activity paradigm has emerged from (research on fibre toxicology) that highlights fibre length, thinness, and biopersistence as major factors in determining the pathogenicity of a fibre."

- K. Donaldson, Crit. Rev. Toxicol. 39 (2009) 487-500

Therefore product stewardship requires extensive characterization

Environmental Defense – DuPont Nano Risk Framework

"A framework to facilitate the responsible development, production, use and disposal of nano-scale materials."

Collaboration begun in October 2005

Objective: A systematic and disciplined process, developed with broad collaboration

- Identify, manage and reduce potential health, safety and environmental risks throughout the lifecycle of such nanomaterials"
- Model and tool for industry, public interest groups, academia and government
- Make available information, tools and methods developed

Framework was published on June 21, 2007

www.nanoriskframework.com

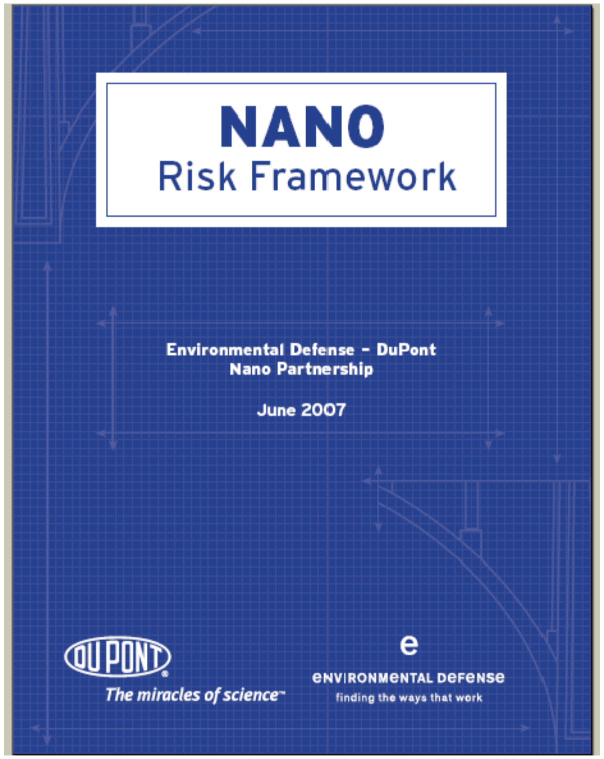
A Mix of Familiar and New Elements

Familiar risk management paradigm

- Development of informational profiles (base sets)
- Information driven
- Reasonable worse case assumptions
- Appropriate bridging
- Applying life cycle thinking

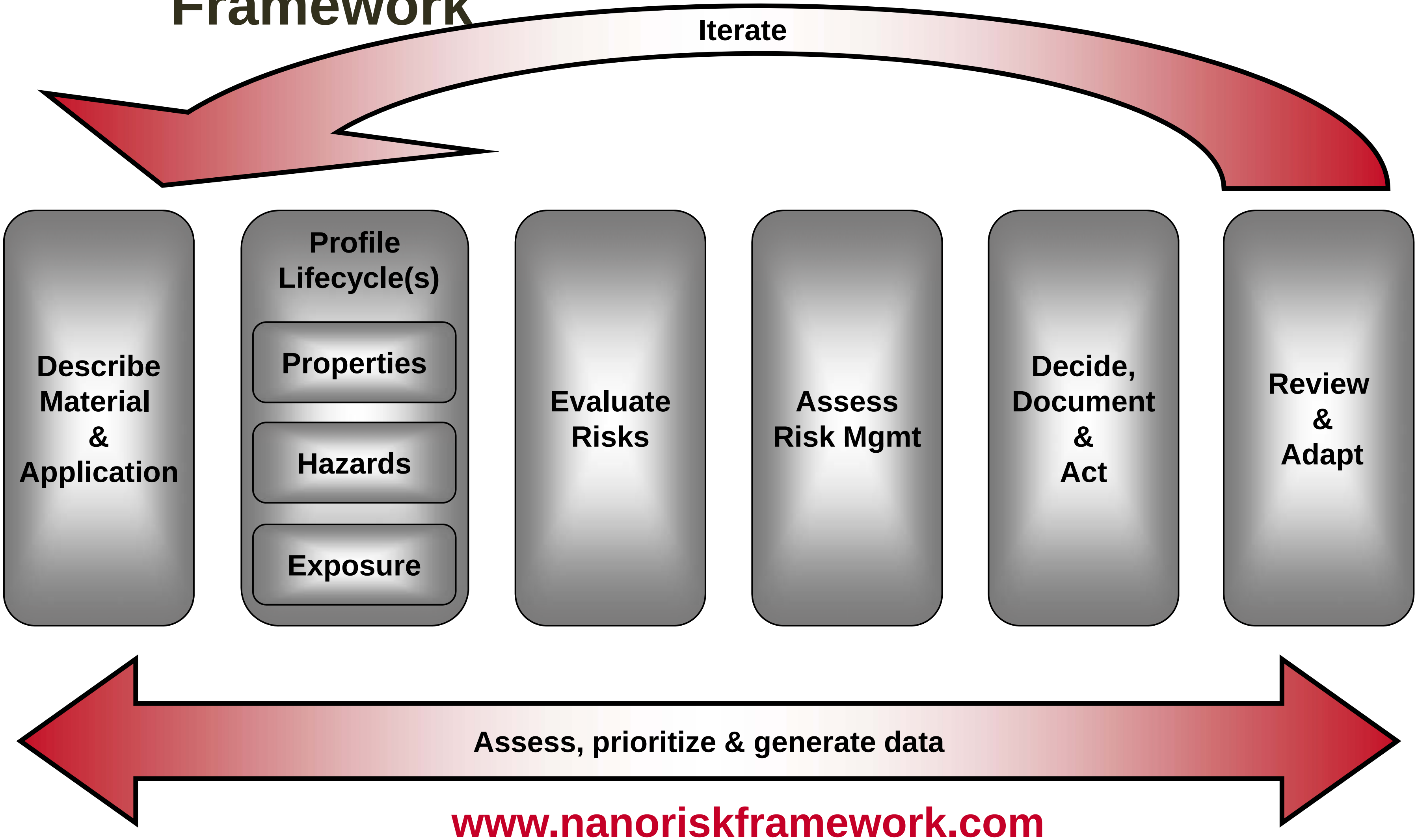
As of 2/1/2011

- Total visits to website – 20,365
- Total Downloads – 9144
- Total Countries – 134



www.nanoriskframework.com

Environmental Defense – DuPont NanoRisk Framework



www.nanoriskframework.com

Environmental Defense – DuPont NanoRisk Framework

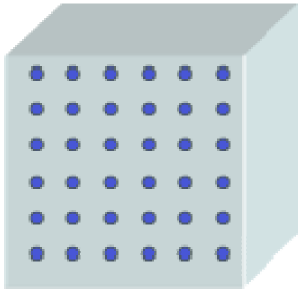
Typical Information

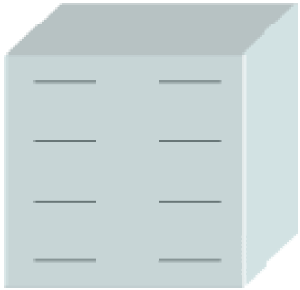
Properties

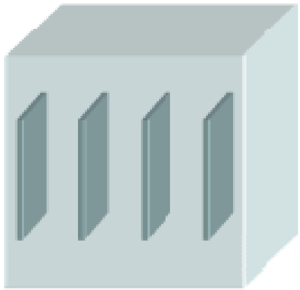
Commercial Name	Particle Size
Technical Name	Size Distribution
Common Form	Surface-Area
Chemical Composition	Particle Density
Molecular Structure	Solubility
Crystal Structure	Dispersability
Physical Form	Agglomeration State
Bulk Density	Chemical Reactivity
	Surface Reactivity
	Porosity
	Surface Charge

Nanocomposite Design Rules: Particle Dimensionality Defines Properties

Properties/uses	
Isotropy, transparency, electronic, magnetic, photonic, model systems	spheres
electrical conductivity, themomechanical, network structures, fillers for fibers	rods
Barrier, thermomechanical, flame retardancy, CTE in plane, very high interfacial area	plates

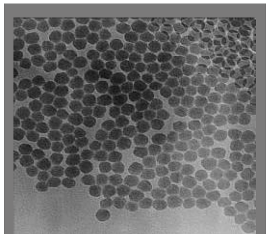




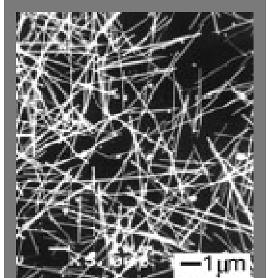


Nanocomposite Systems Require Compatible Particles, Polymers and Processes

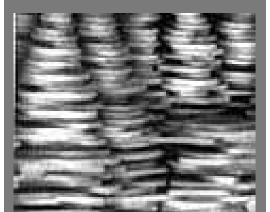
Nanoparticles



TiO_2, SiO_2, $BaTiO_3$, AlN, diamonds, Q-dots, polymers…



CNT, Al_2O_3, SiC, TiO_2 tubes….



Clay, exfoliated graphite..

Dispersion & Compatibilization

Interfacial Chemistry
- Surfactants
- Coupling agents

Structures & Interphase
- Dendrimers
- Multiblock polymers
- Flexible links

Process Technology
- Polymer processing
- Milling/grinding
- Particle formation/modification

Polymers

Polyimide

Fluoropolymers

Thermoset

Polyamide

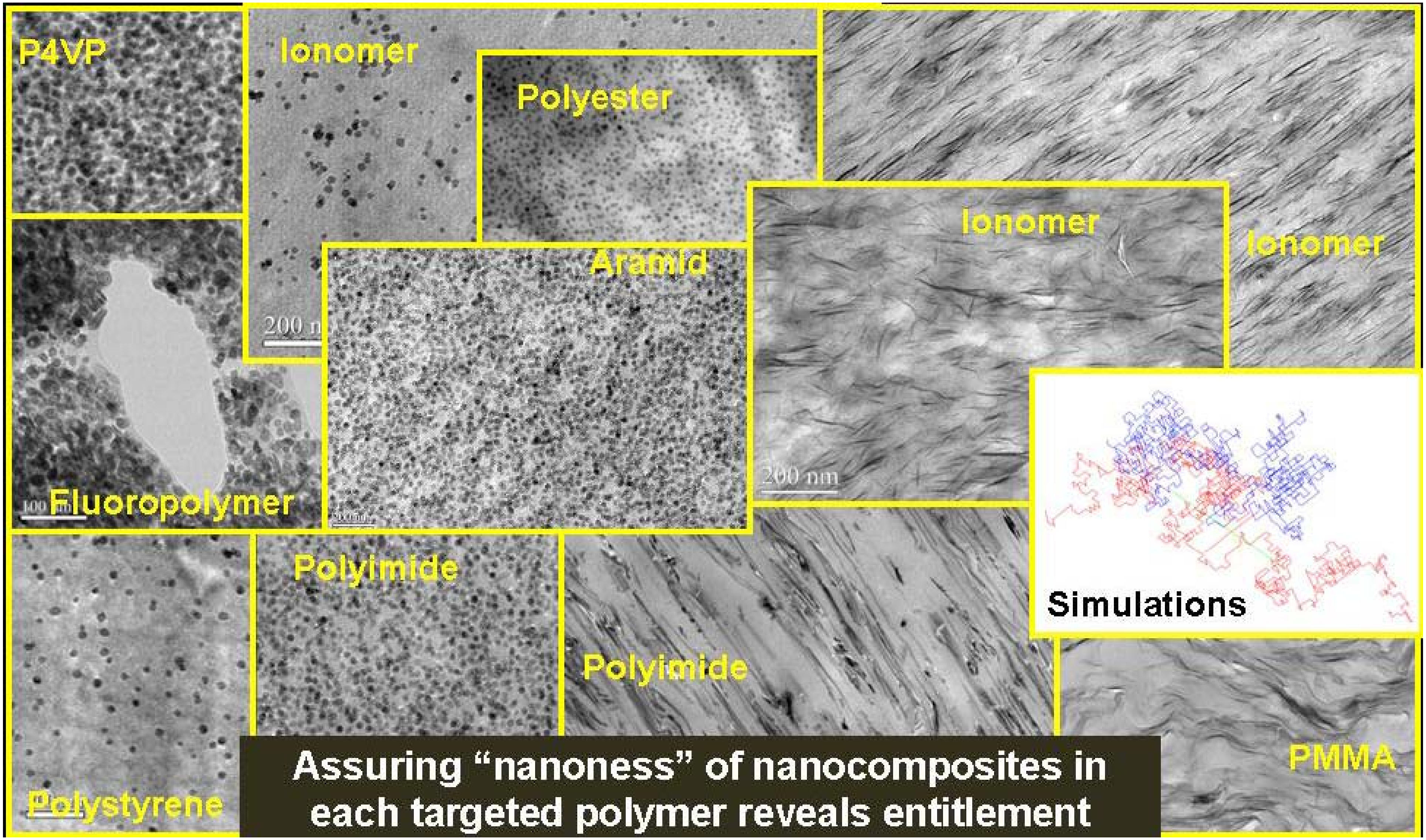
Polyester

Polyolefins

Ionomers

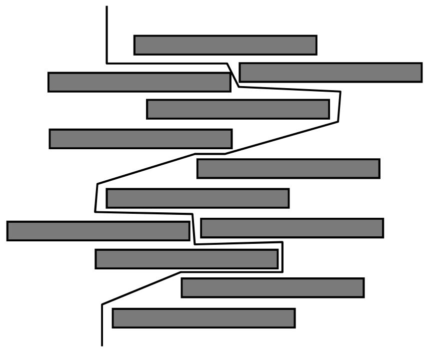
Others…

Processes Developed to Create Excellent Dispersions in Multiple Polymers

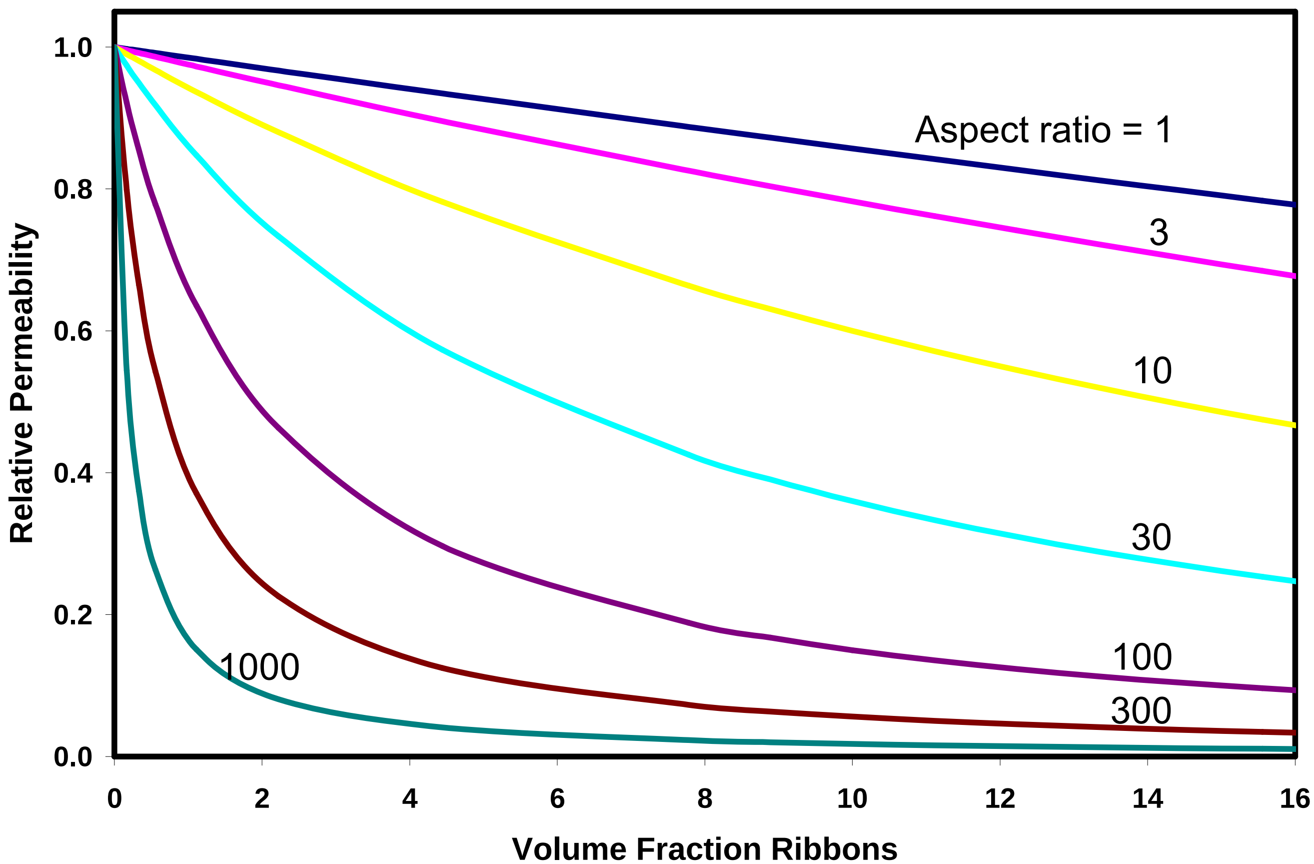


Diffusion Barrier vs. Filler Aspect Ratio (Nielsen Model)

Tortuous Path Model

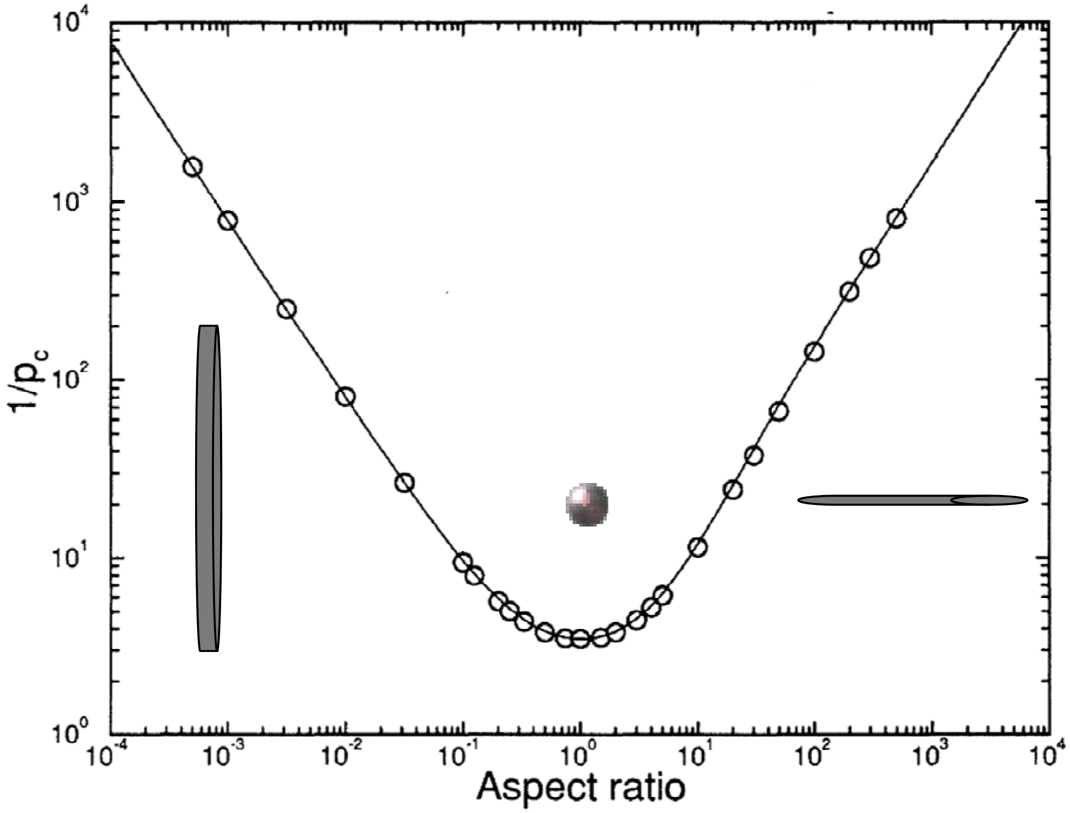


Aspect ratio = t/w



After L.E. Nielsen,
Journal of Macromolecular Science, Part A, **1** (1967) 929 - 942

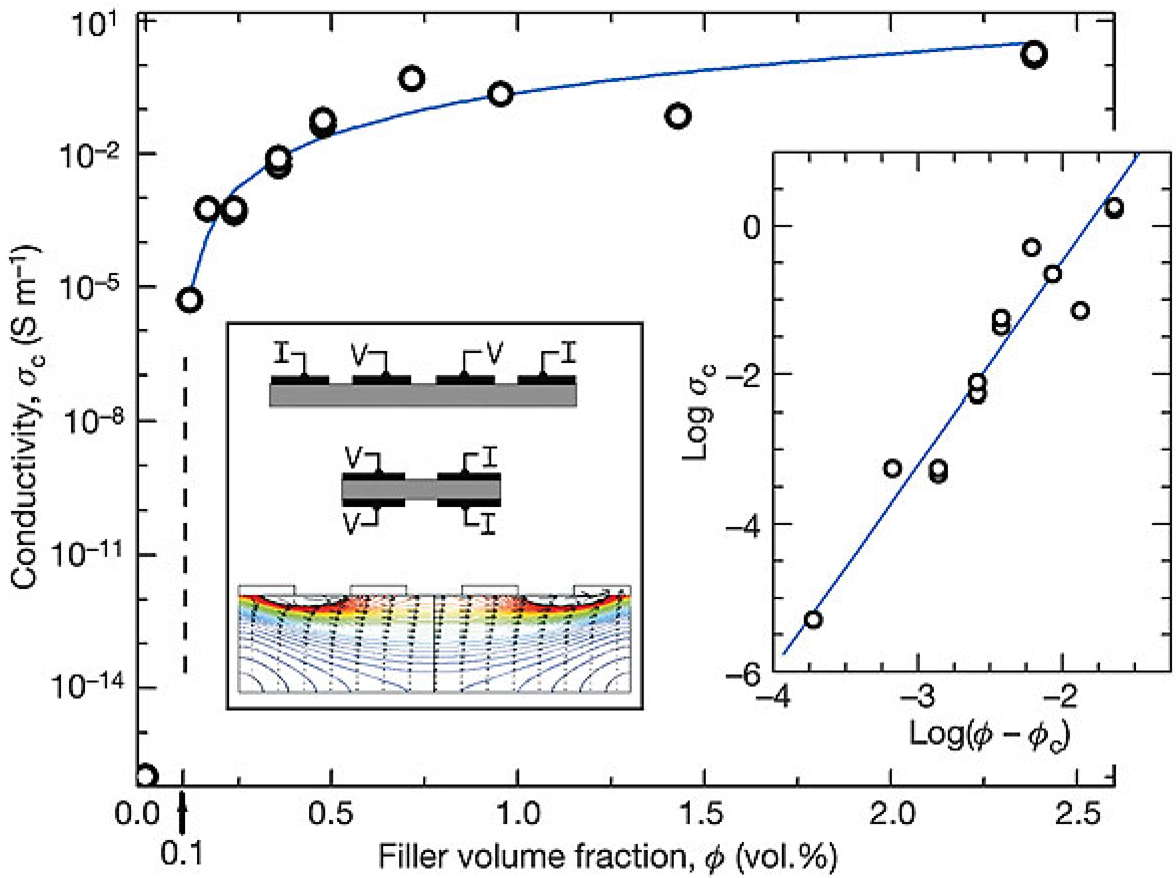
Percolation Threshold to Aspect Ratio (Garboczi Model)



$P_c \equiv$ critical volume fraction for ellipsoid percolation

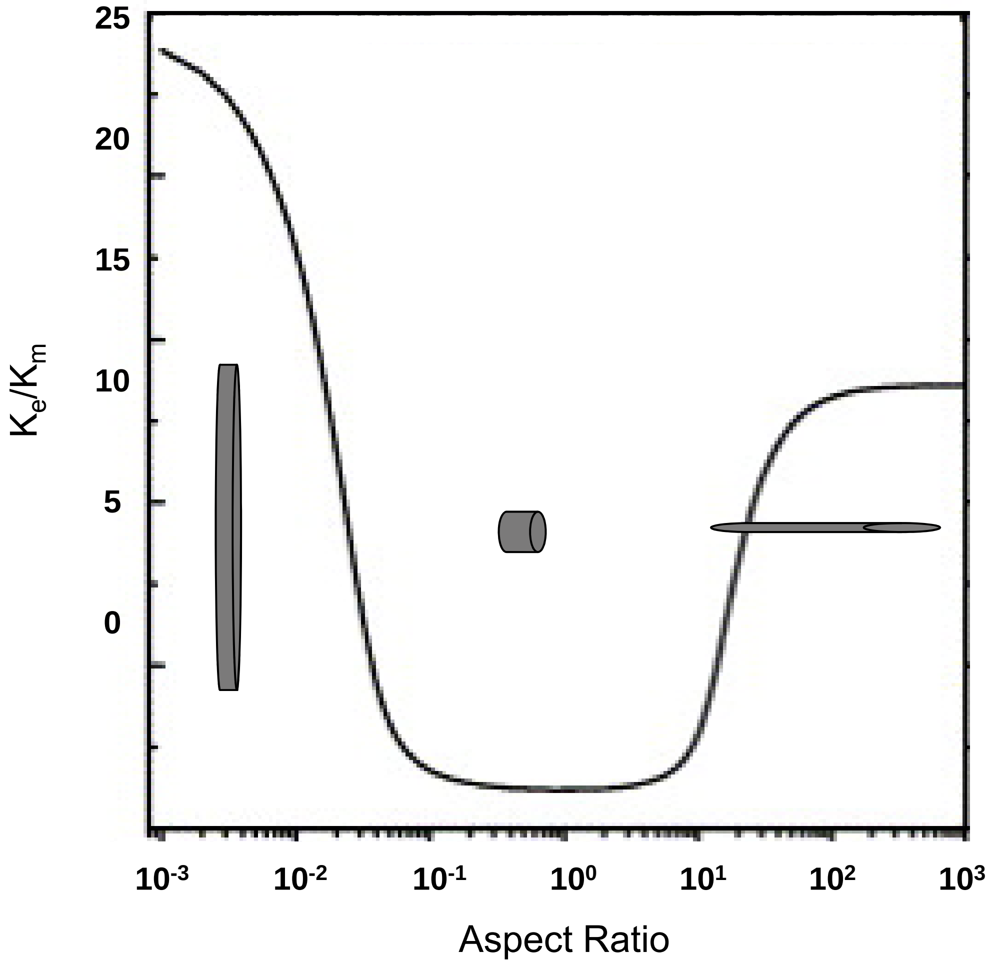
E.J. Garboczi, et. al.,
Physical Review E, **52** (1995) 819-828

Graphene/Polystyrene Electrical Conductivity Fits Garboczi Model



S. Stankovich, et. al.,
Nature **442** (2006) 282-286

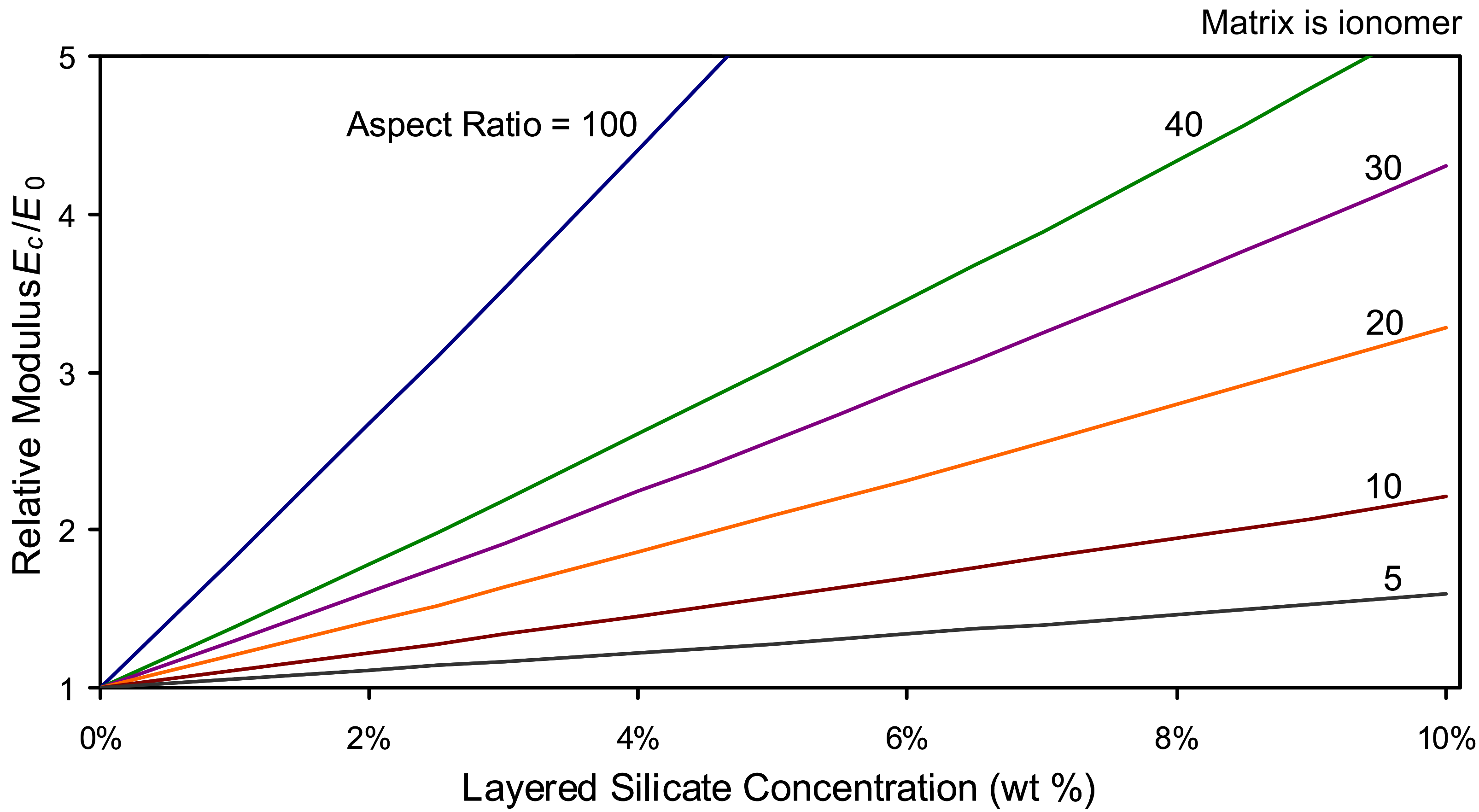
Thermal Conductivity vs. Aspect Ratio (Gao Model)



Volume fraction = 0.05
K_p/K_m = 1000
Contact resistance = 0

L. Gao, et. al.,
Chemical Physics Letters, **434** (2007) Pages 297-300

Elastic Modulus to Filler Aspect Ratio (Halpin-Tsai)



After J.C. Halpin, et. al.,
Polymer Engineering and Science, **16** (1976) 344-352

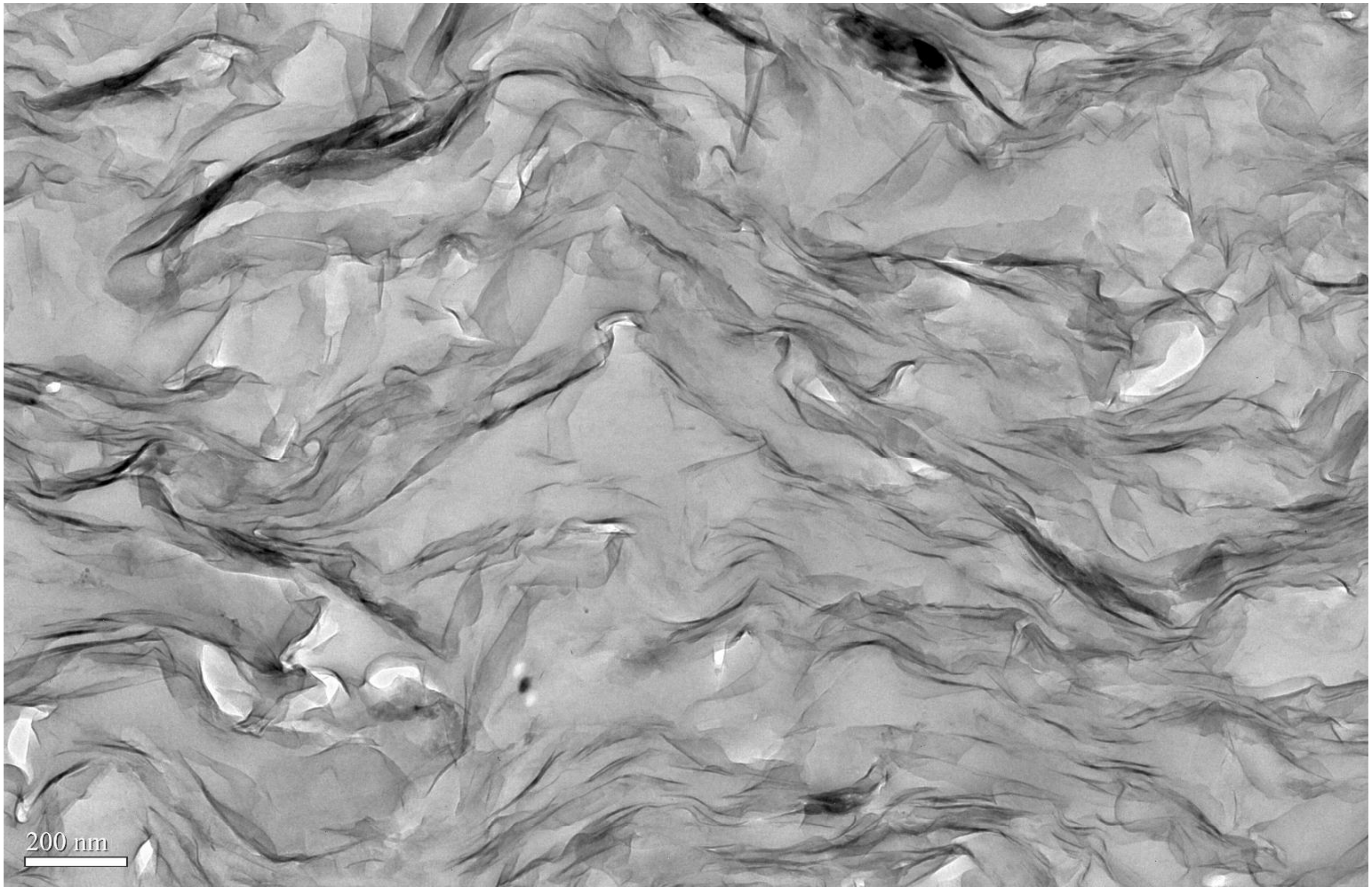
Techniques for Measuring Nanoparticle Size

Method	Dry/Solvent Dispersed			Composite		
	Plates	Spheres	Rods	Plates	Spheres	Rods
Surface Area (BET)		🟢				
Static Light Scattering (SLS)		🟢		🟡	🟢	🟡
Dynamic light scattering (DLS)		🟢				
Scanning Electron Microscopy (SEM)	🟡	🟢	🟡			
Transmission Electron Microscopy (TEM)	🟡	🟢	🟡	🟡	🟢	🟡
Scanning Probe Microscopy (SPM)	🟡	🟢	🟡			
Small Angle X-ray Scattering (SAXS)	🟡	🟢	🟡	🟡	🟢	🟡

Techniques for Measuring Nanoparticle Size

Method	Composite						
	Plate	Sphere	Rod	Distri-bution	Multi-modal	Faceted	Re-entrant
Surface Area (BET)							
Static Light Scattering (SLS)	🟡	🟢	🟡				
Dynamic light scattering (DLS)							
Scanning Electron Micr. (SEM)							
Transmission Electron Micr. (TEM)	🟡	🟢	🟡				
Scanning Probe Micr. (SPM)							
Small Angle X-ray Scattering (SAXS)	🟡	🟢	🟡				

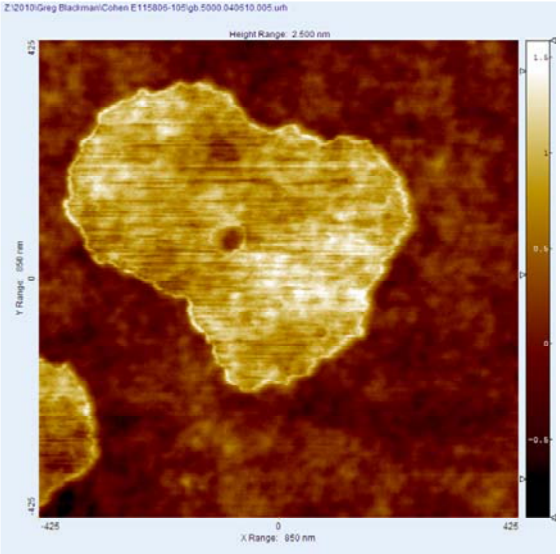
Electron Microscopy can be Ambiguous



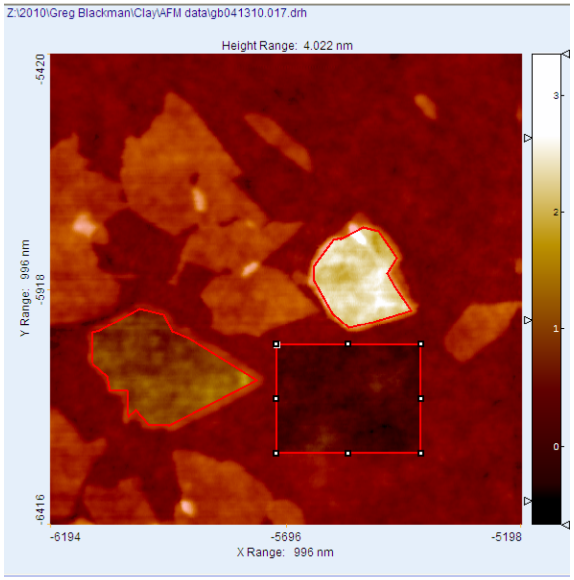
5 v% clay in PMMA

Individual Clay Sheets ARE Irregular

Height images (AFM)



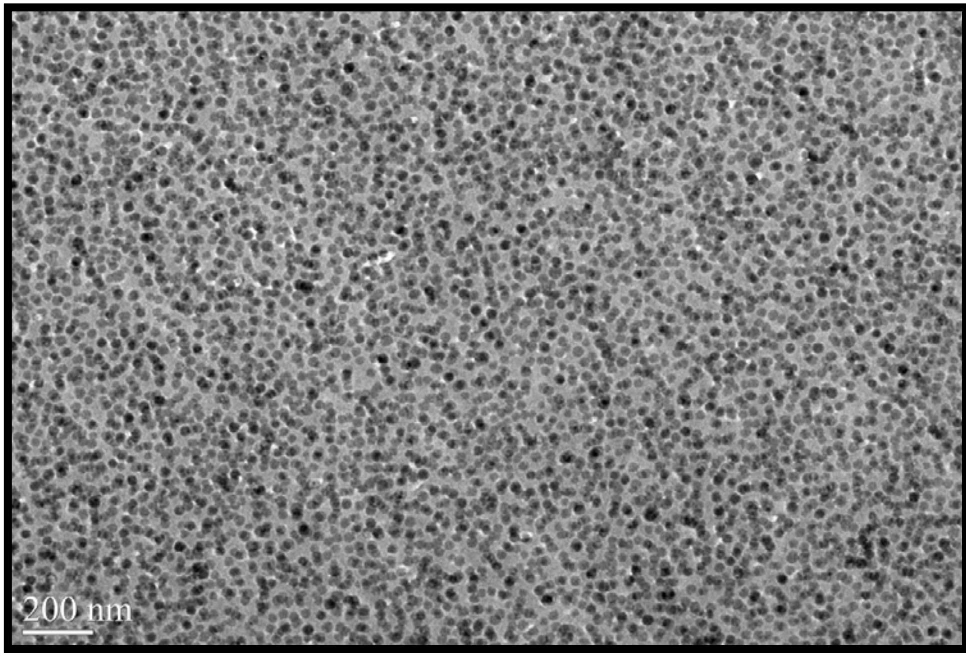
Laponite



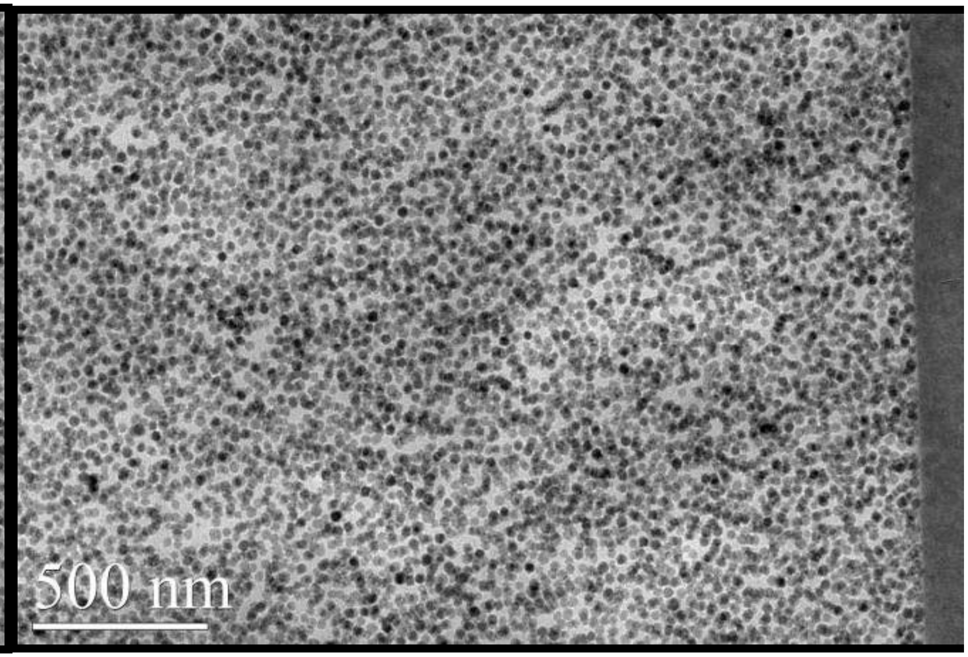
Montmorillonite

Images courtesy of Greg Blackman

Are These Microstructures Different?

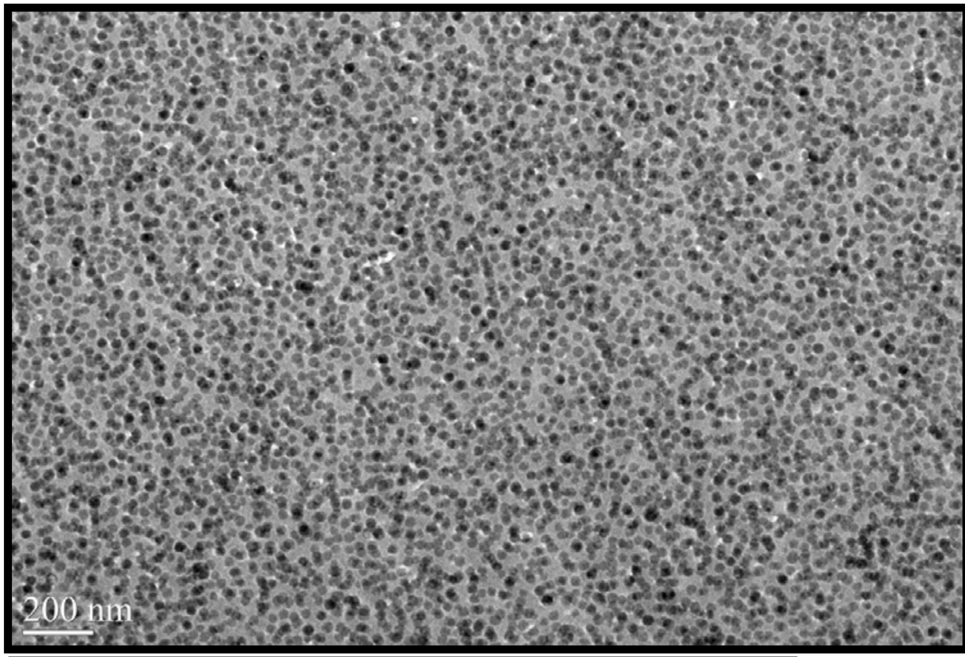


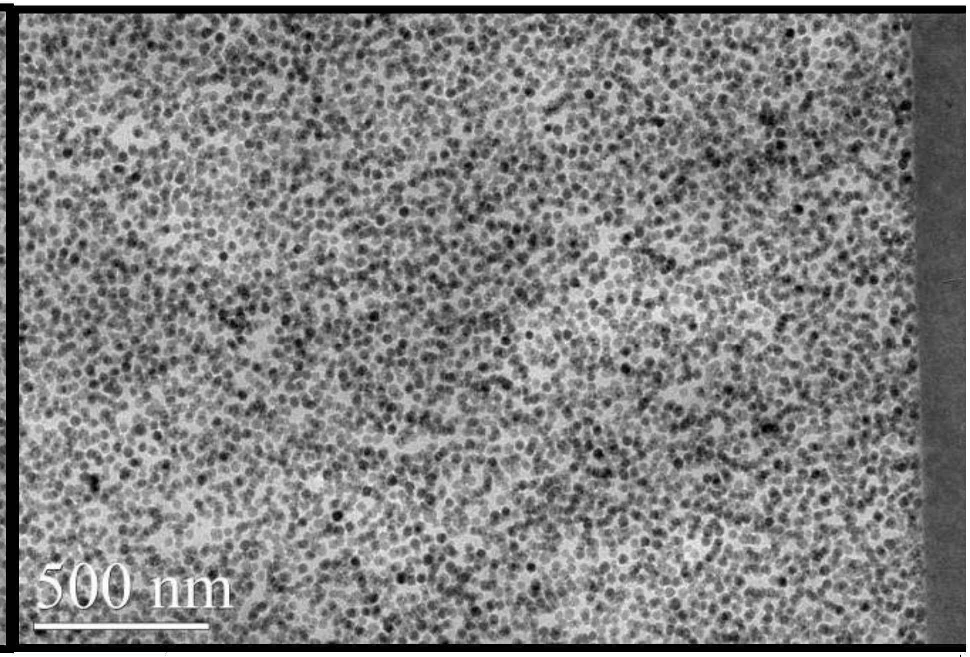
Silica in polystyrene (10%)

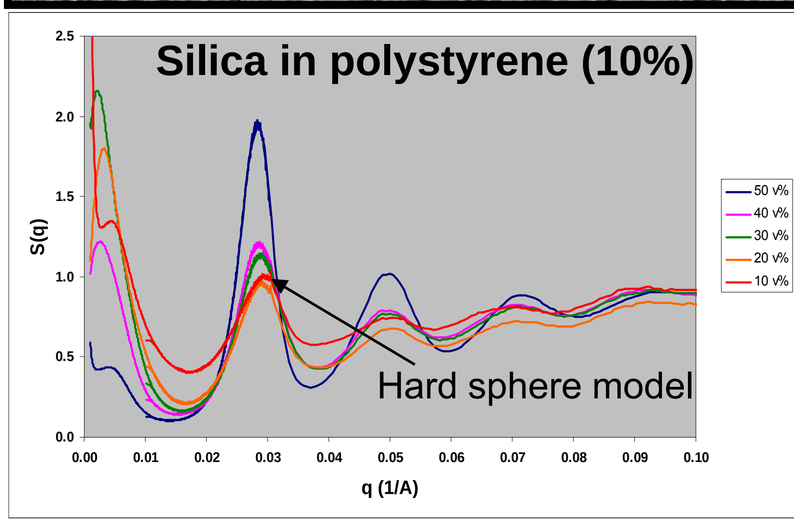


Silica in PMMA (10%)

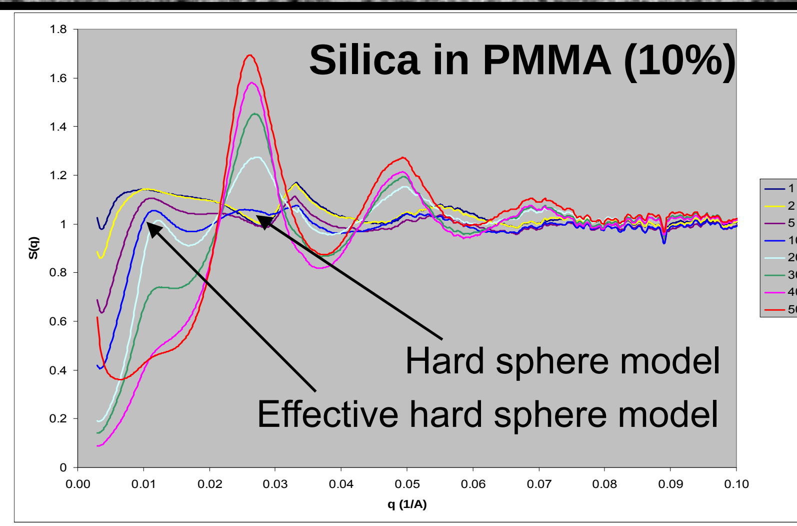
Need to Measure the Spaces (Dispersion)!







SAXS Data



Nanoparticle Characterization Required for Product Stewardship, Property Understanding

NanoRisk Framework is rigorous and data driven assessment tool

- Materials and application descriptions
- Lifecycle profiles
- Risk evaluation and Management
- Decide, document and act
- Review and adapt

Nanoparticle characterization is a fundamental part of the product stewardship process

Protecting people and environment is our highest priority

www.nanoriskframework.com

Nanoparticle Characterization is Required for Understanding Property Development

Particle size, shape, distribution responsible for properties

Characterization of platy and rod-like particles onerous at best

- Best done in highly oriented systems and low particle concentrations
- This is rarely the case in nanocomposites

Characterization almost impossible in nanocomposites

- Size distributions (especially multimodal)
- Faceted particles
- Highly irregular particles (especially re-entrant shapes)
- High loadings

Dispersion very important also

- But is the subject of another (lengthy) discussion