

# POLYMER AND COMPOSITE MATERIALS PROCESSING

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# Ch. 7. Nanomaterials & Nanocomposites Processing

## 7.1. What is nanotechnology?

- Understanding and control of matter **at dimensions of roughly 1 to 100 nanometers, where unique phenomena** enable novel applications
- **At this level, the physical, chemical, and biological properties of materials differ** in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter

## 7.2. Why is this length scale so important?

- Quantum mechanical properties of electrons inside matter
- **Atomic interactions are influenced by materials variations on the nm scale**
- By creating nm scale structures, it is possible **to control the fundamental properties of materials**, such as melting temperature, magnetic properties, charge capacity, and even their color
- Nanoscale structures such as nanoparticles and nanolayers: **very high surface-to-volume and aspect ratio**, making them ideal for use in polymeric materials

### 7.3. What does *Nano* really mean?

- One billionth of a meter ( $10^{-9}$  m), about four times the diameter of an atom
- e.g. a human red blood cell = 10,000 nm, a cell of *E. coli* = 1000 nm, a polymer coil = 40 nm, Quantum-dot = 7 nm

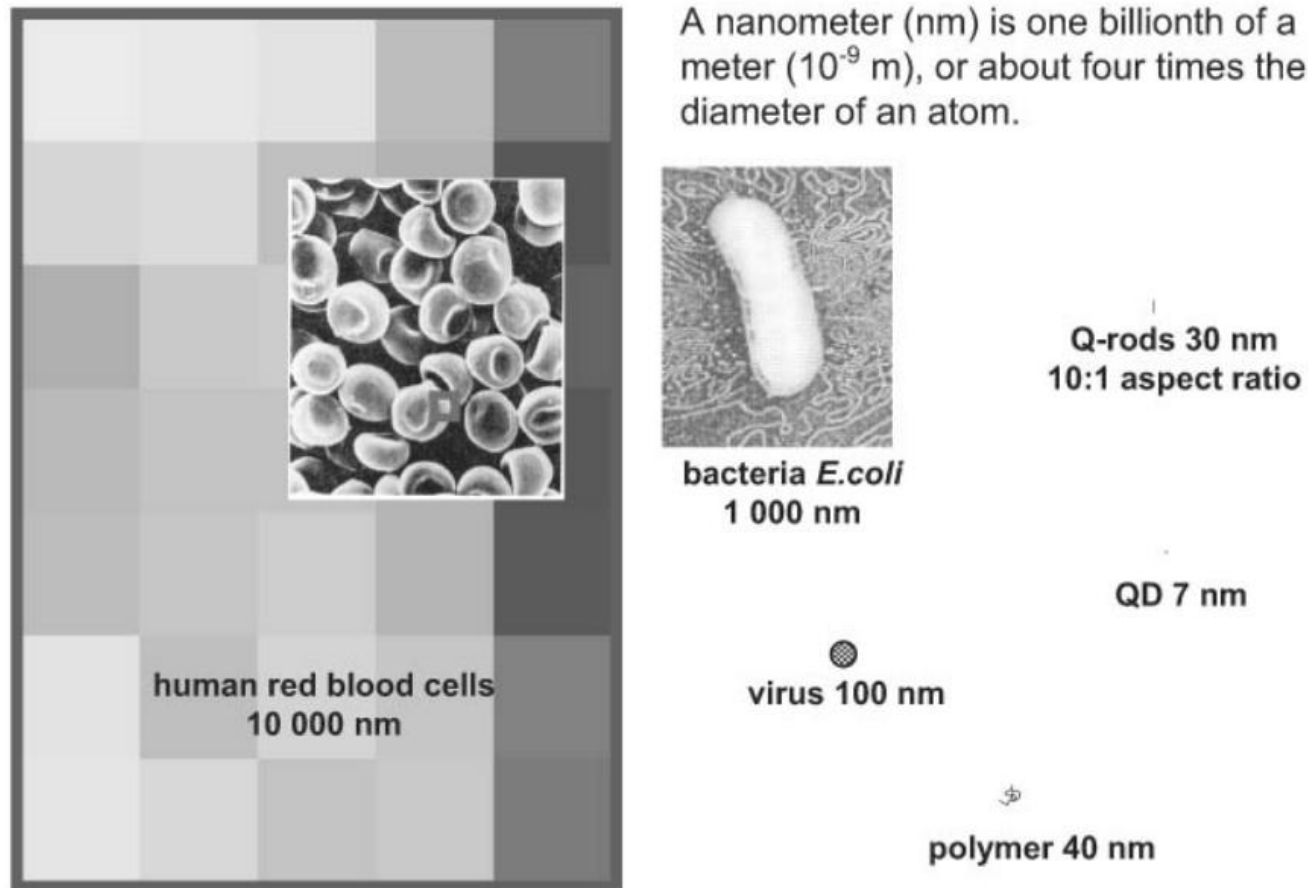
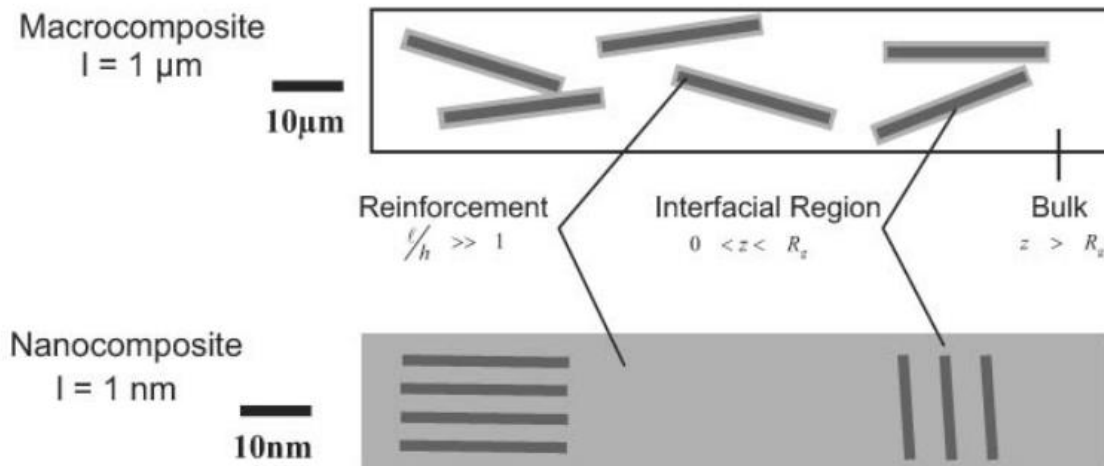


Figure 1.1 What *nano* really means. (Courtesy of R. Vaia.)

## 7.4. Uniqueness of nanostructured materials

- If the length scale of polymer fillers is in micrometers:
    - : The reinforcement length scale is in micrometers
    - The interface of fillers is close to the bulk polymer matrix
  - If the length scale of the reinforcement is in nanometer scale
    - : Ultra large interfacial area per volume
    - The distances b/t the polymer and filler components are extremely short
- e.g. Polymer coils  $\sim 40$  nm, the nanoparticles are on the same order  
→ Molecular interaction is enhanced



### Characteristic

Ultralarge interfacial area per volume  
High fraction interfacial (interphase) material  
Short distances between components

Nanopolymer Nanoinorganic

Hierarchical  
Morphology  
Control  
Nano, Meso, Micro

Figure 1.2 Uniqueness of nanostructured materials. (Courtesy of R. Vaia.)

## 7.5. Polymer nanomaterials

- Nanomaterials can be classified into *nanostructured materials* and *nanophase/nanoparticle materials*.
- Nanostructured materials : condensed bulk materials made of nanometer size grains (agglomerates)
- Nanophase/nanoparticle materials: dispersive nanoparticles in a medium
- Polymer nanocomposites (PNs) : multifunctional, high-performance polymers filled with nanomaterials
  - Multifunctional features : thermal resistance, flame resistance, moisture resistance, decreased permeability, charge dissipation, chemical resistance, etc.
- Incorporation of nanoparticles into selected polymer matrix systems need *surface-treatment of nanoparticles* to provide hydrophobic characteristics
- *Uniform dispersion of nanoparticles* produces ultra large interfacial area.
- Polymer nanocomposites (PNMs) do not refer to conventional fiber-reinforced polymer composites.
  - PNMs may provide matrix resins with “*multifunctionality*” and is not based solely on mechanical enhancements of the neat resin

## 7.6. Current polymer nanocomposite technology

- The nanoparticle has at least one dimension in nanometer scale.
- PNPs show major improvements in mechanical properties, gas barrier properties, thermal stability, fire retardancy, and other areas.
- Facts affecting PNPs properties
  - Synthesis methods such as melt compounding, solvent blending, in-situ polymerization, emulsion polymerization, etc
  - Polymer nanocomposite morphology
  - Types of nanoparticles and their surface treatments
  - Polymer matrix such as crystallinity, MW, polymer chemistry, thermoplastic or setting

## 7.7. Different types of nanoparticles

- Depending on the applications, the research must determine the type of nanoparticle.
- Commonly used nanoparticles in the literature :
  - Montmorillonite organoclays (MMT)
  - Carbon nanofibers (CNFs)
  - Polyhedral oligomeric silsesquioxane (POSS<sup>®</sup>)
  - Carbon nanotubes [multiwall (MWNTs), small-diameter (SDNTs), and single-wall (SWNTs)]
  - Nanosilica (N-silica)
  - Nanoaluminum oxide ( $\text{Al}_2\text{O}_3$ )
  - Nanotitanium oxide ( $\text{TiO}_2$ )
  - Others

**TABLE 2.1 Characteristics of Nanoparticles to Polymers**

Improved properties	Disadvantages
<ul style="list-style-type: none"><li>■ Mechanical properties (tensile strength, stiffness, toughness)</li><li>■ Gas barrier</li><li>■ Synergistic flame retardant additive</li><li>■ Dimensional stability</li><li>■ Thermal expansion</li><li>■ Thermal conductivity</li><li>■ Ablation resistance</li><li>■ Chemical resistance</li><li>■ Reinforcement</li></ul>	<ul style="list-style-type: none"><li>■ Viscosity increase (limits processability)</li><li>■ Dispersion difficulties</li><li>■ Optical issues</li><li>■ Sedimentation</li><li>■ Black color when different carbon containing nanoparticles are used</li></ul>

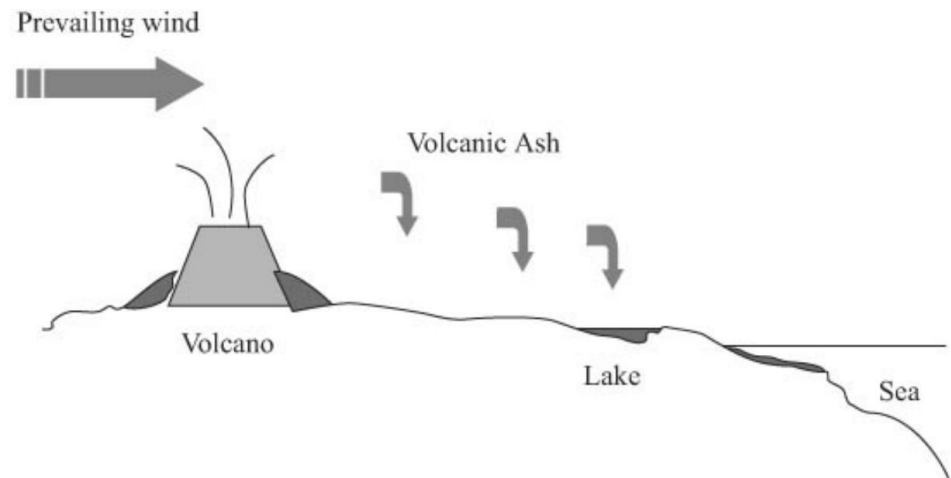
## 7.7.1 Montmorillonite (MMT) nanoclays

- Origin

- Nanoclay is the most widely investigated nanoparticle in a variety of different polymers.
- Most commonly formed by the in-situ alteration of volcanic ash.
- Clay soil has particle size of less than  $2\ \mu\text{m}$ .
- Bentonite : contains MMT, glass, mixed-layer clays, quarts, zeolite, carbonates, etc.



**Figure 2.1** Bentonite comes from the deposition and alternation of volcanic ash from inland sea beds from 85 million years ago.



**Figure 2.2** Formation of natural clays by the in-situ alteration of volcanic ash.



- Structure

- Sheet structure consisting of layers of tetrahedral silicate layer and octahedral alumina layer
- One clay sheet has a thickness of 0.96 nm.
- The chemical formula of the MMT clay is  $\text{Na}_{1/3}(\text{Al}_{5/3}\text{Mg}_{1/3})\text{Si}_4\text{O}_{10}(\text{OH})_2$

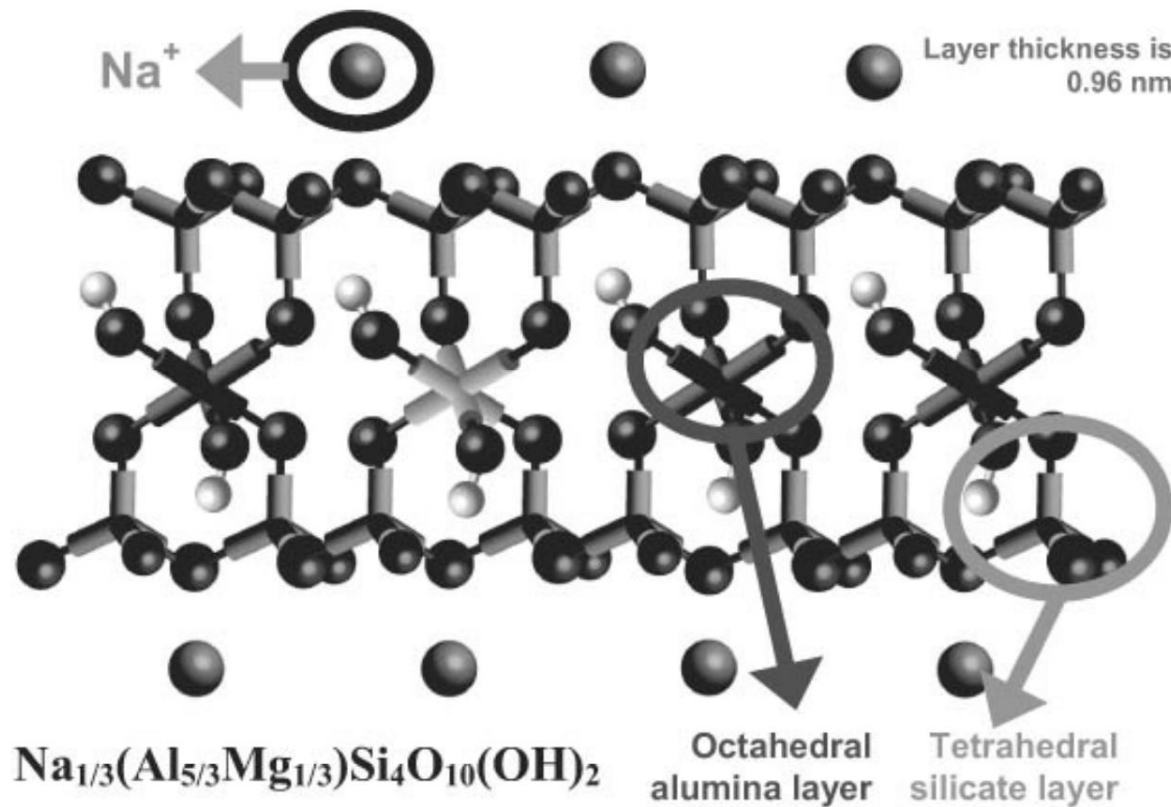
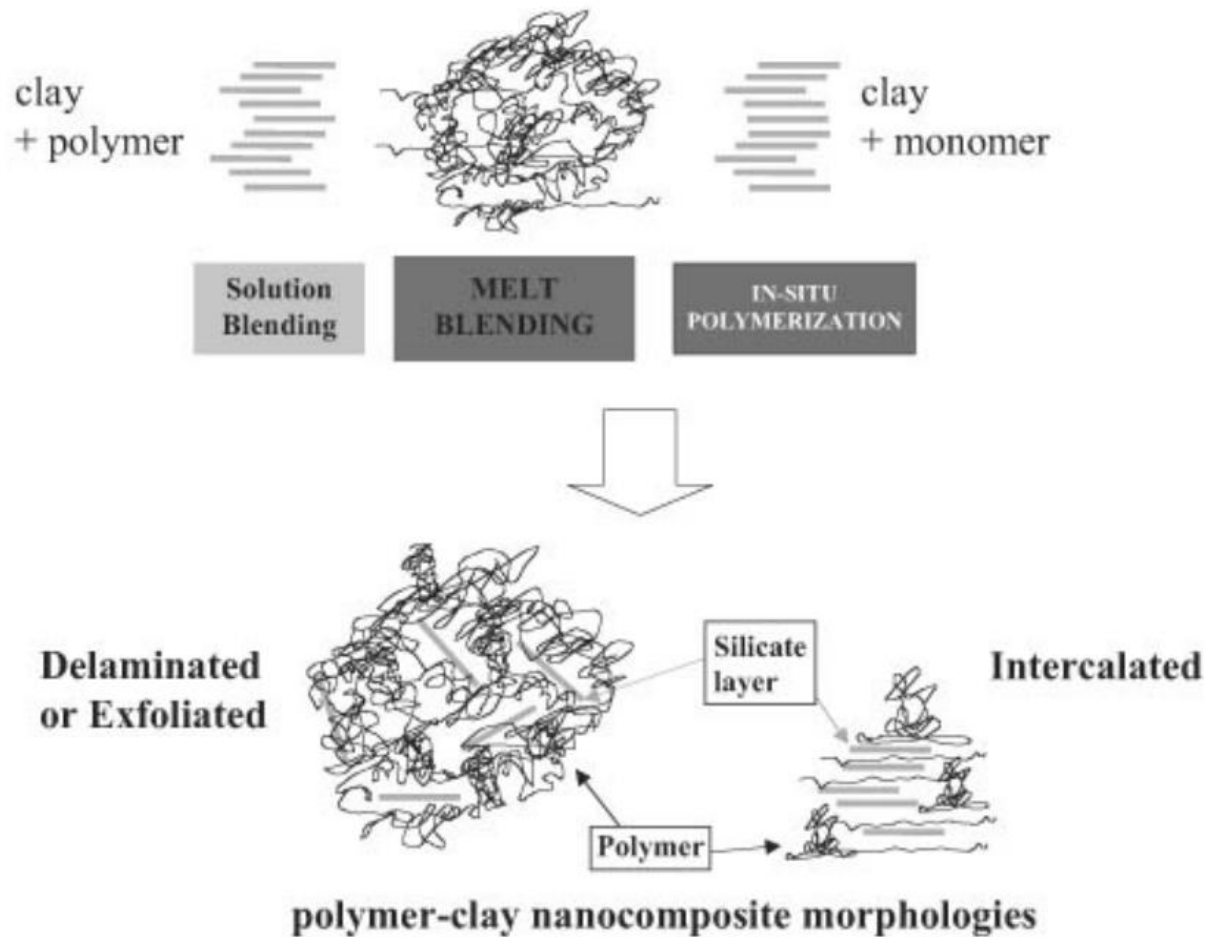
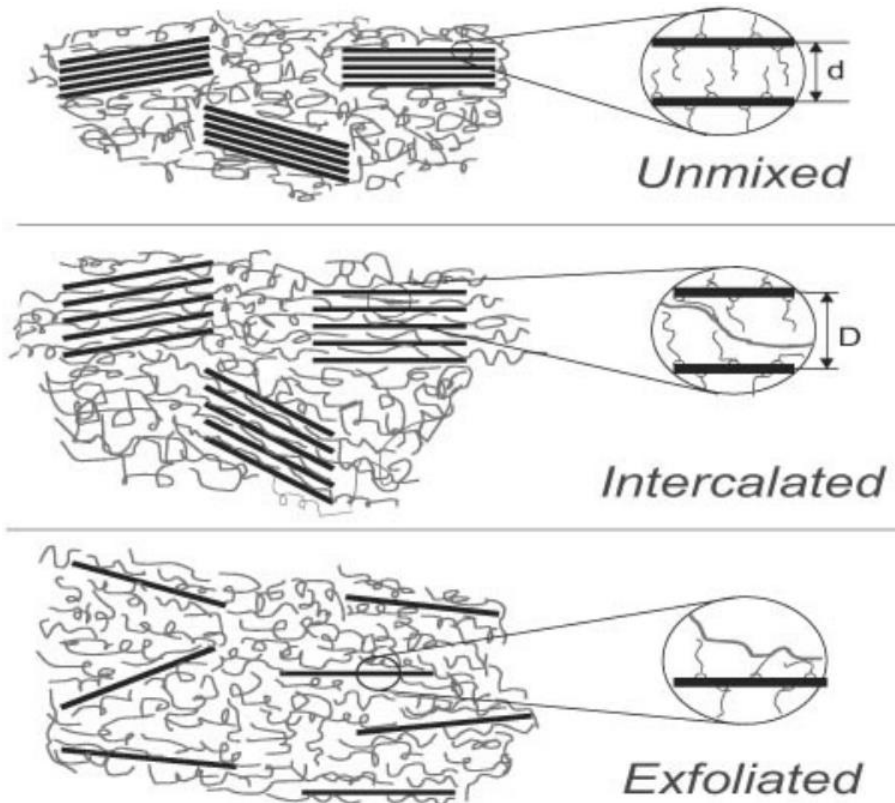


Figure 2.3 Chemical structure of montmorillonite nanoclays.

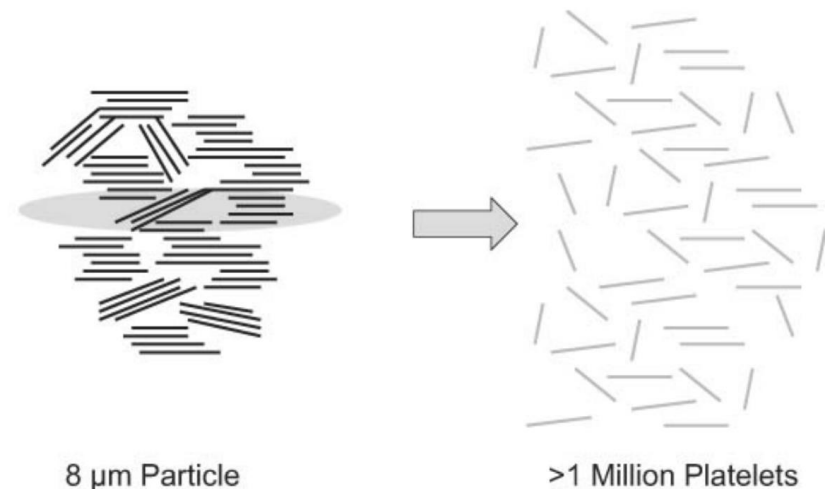
- 2D materials dispersion : Importance of organic treatment
  - Since layered silicates : hydrophilic materials, they **must be made hydrophobic (organophilic)** to become compatible with most polymers that are hydrophobic.
  - Without organic treatment, layer silicates will only disperse and phase separate.



- Dispersing nanoclay
  - solution blending, melt blending, or in-situ polymerization processes.
  - Polymer-clay nanocomposites can be classified morphologically into 3 states :
    - (a) unmixed, (b) intercalated, (c) exfoliated (delaminated)
  - The most desirable morphological state : exfoliation > intercalation > unmixed
  - The processing challenge of nanoclay to disperse the 8  $\mu\text{m}$  particles into > 1 million platelets.



**Figure 2.5** Schematic showing polymer-clay nanocomposite classifications.



**Figure 2.6** The processing challenge of nanoclay is turning 8- $\mu\text{m}$  particles into > 1 million platelets. (Courtesy of SCP.)

- Dispersion mechanism : (a) chemistry route as with in-situ polymerization
- (b) processing route as with extrusion
- (c) combining the chemistry and the processing routes  
(the optimal way)

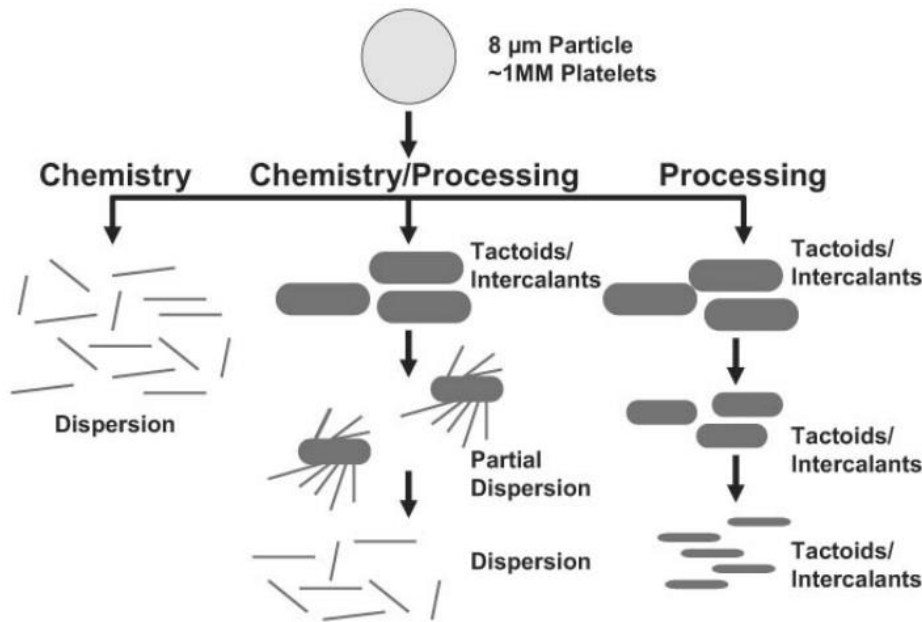


Figure 2.7 Different mechanisms for dispersing nanoclays. (Courtesy of SCP.)

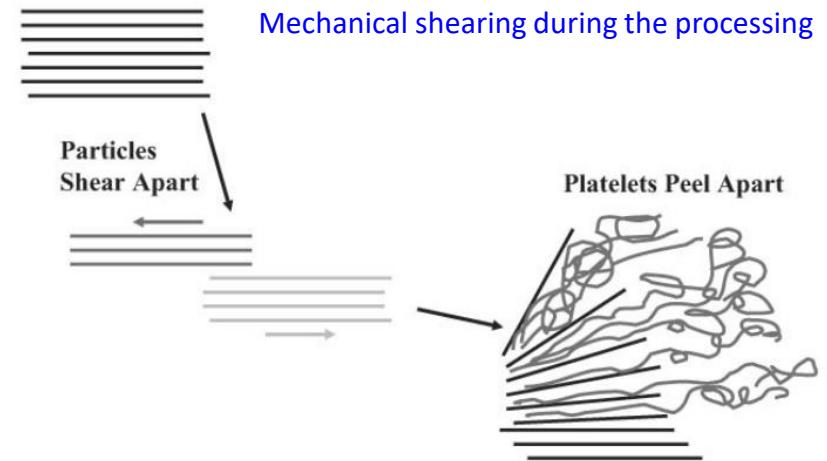
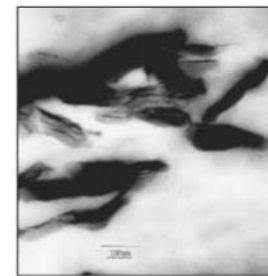
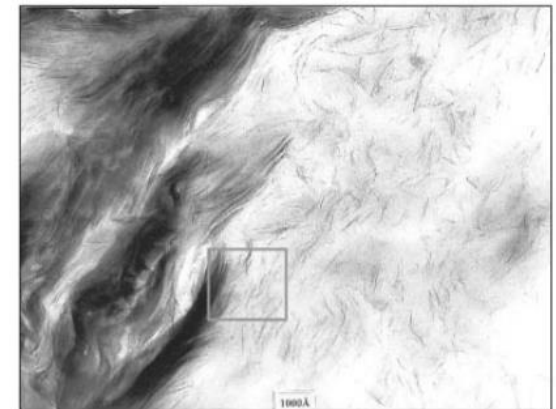


Figure 2.8 Cartoon showing particles shearing and platelets peeling apart. (Courtesy of SCP.)



Particles Shear Apart



Platelets Peel Apart

Figure 2.9 TEM micrographs showing particles shearing and platelets peeling apart. (Courtesy of SCP.)

- Cloisite (commercial name) additives
  - Organoclays are surface modified to allow complete dispersibility and miscibility.
  - Many clays are surface treated and commercially produced in market
  - *Cloisite Na<sup>+</sup>* : natural MMT
    - improves heat deflection temperature (HDT), thermal expansion coefficient (CTE), and gas barrier properties
  - *Cloisite 15A* and *20A* : natural MMT modified with a quaternary ammonium salt
  - .....

**TABLE 2.2 Properties of Several SCP Cloisite MMT Clays**

MMT clay/ properties	Organic modifier <sup>#</sup>	Cation exchange capacity (meq/100g clay)	% Moisture	% Weight loss on ignition	X-ray results d <sub>001</sub> (Å)
Cloisite Na <sup>+</sup>	None	92.6	<2%	7%	11.7
Cloisite 15A	2M2HT (1)	125	<2%	43%	31.5
Cloisite 20A	2M2HT (1)	95	<2%	38%	24.2
Cloisite 30B	MT2EtOT (2)	90	<2%	30%	18.5
Cloisite 93A	M2HT (3)	90	<2%	40%	23.6
Cloisite 25A	2MHTL8 (4)	95	<2%	34%	18.6
Cloisite 10A	2MBHT (5)	125	<2%	39%	19.2

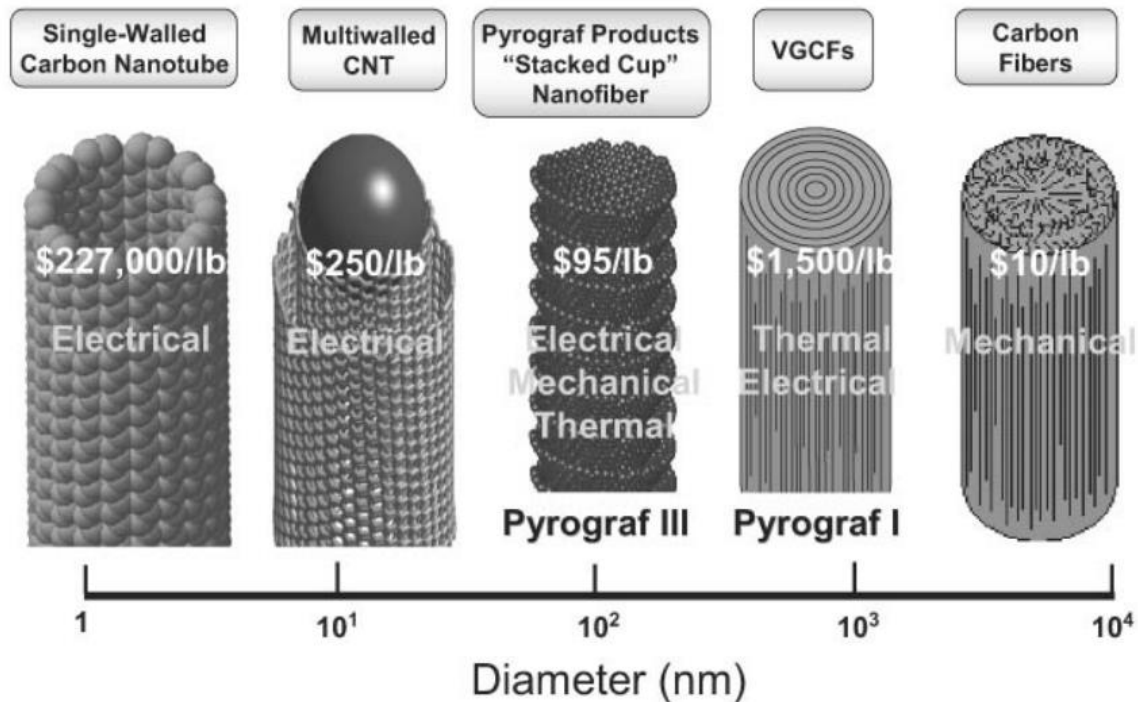
<sup>#</sup> See TABLE 2.3 for chemical data



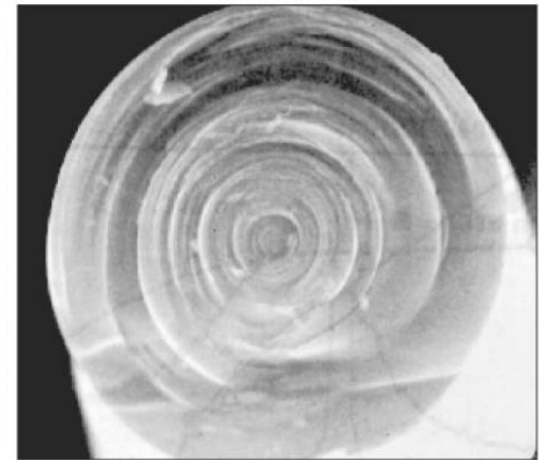
## 7.7.2 Carbon nanofibers (CNFs) – vapor grown carbon fibers (VGCFs)

- Origin

- Vapor-grown carbon fiber produced in the gas phase from the pyrolysis of hydrocarbons
- CNFs have transport and mechanical properties that approach the theoretical values of single-crystal graphite.



**Figure 2.10** Sizes and costs from single-wall carbon nanotubes to conventional carbon fibers. (Courtesy of ASI.)



**Figure 2.12** TEM micrographs of Pyrograf-I VGCF. (Courtesy of ASI.)

- Properties

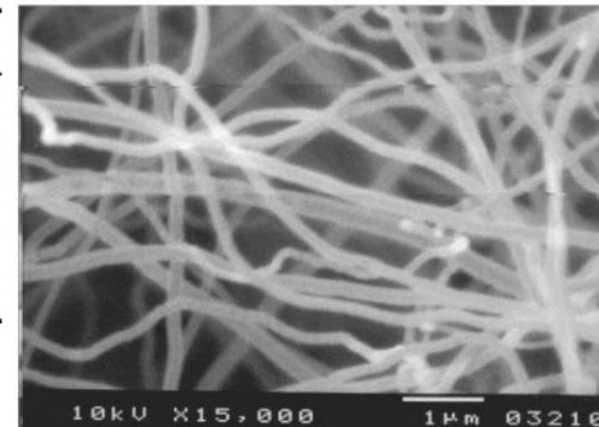
- Vapor-grown carbon fiber produced in the gas phase from the pyrolysis of hydrocarbons
- CNFs have transport and mechanical properties that approach the theoretical values of single-crystal graphite.
- One of the goals for the broad utility of CNFs is to provide mechanical reinforcement and **low-cost composite fabrication methods** such as injection molding.

- Depending on fabrication methods, fiber filling efficiency and mechanical properties are varied
- **Composite fabrication methods** and **fiber reinforced composites theories** will be learned. (for a light-weight purpose, especially CF or GF reinforced composites are normally used)

**TABLE 2.6 Properties of CNFs**

Property (units)	As grown	Heat treated
Tensile strength (GPa)	2.7	7.0
Tensile modulus (GPa)	400	600
Ultimate strain (%)	1.5	0.5
Density (g/cc)	1.8	2.1
Electrical resistivity ( $\mu\Omega\text{-cm}$ )	1000	55
Thermal conductivity (W/m-K)	20	1950

After graphitizing heat treatment to 3000 °C



**Figure 2.13** SEM micrograph showing Pyrograf-III carbon nanofibers in bundles. (Courtesy of ASI.)

- Properties

- CNF nanocomposites can offer multifunctional performance for several potential aerospace and other commercial applications :

- EMI shielding, electrostatic painting, antistatic
    - Thermal conductivity of spacecraft, batteries, and electronics
    - Improved mechanical properties in polymers (composite structure, injection-molded parts, tires)
    - Reduced coefficient of thermal expansion (CTE) for spacecraft resin systems



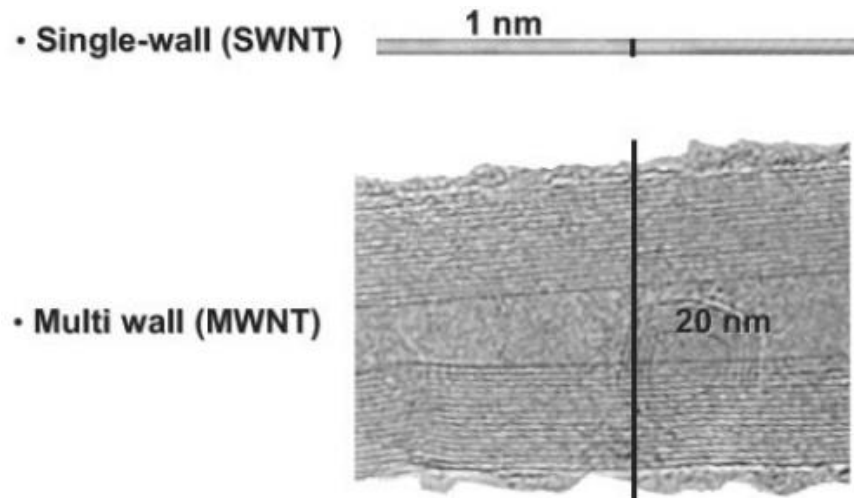
## 7.7.3 Carbon nanotubes

- Properties

- Carbon nanotubes are excellent candidates for **stiff and robust structures because the carbon-carbon bond in the graphite** is one of the strongest in nature.
- Thermal conductivity of carbon nanotubes can be extremely high.

- Classifications

- single-wall (SWNT), multiwall (MWNT), small diameter (SDNT) based on the number of walls in the carbon nanotubes
- SWNT has about 1 nm in diameter with  $\mu\text{m}$  in length, MWNT 20 – 70 nm in diameter and 50  $\mu\text{m}$  in length



**Figure 2.22** Definition of single- and multiwall carbon nanotubes.  
(Courtesy of CNI.)

- Comparison : SWNT v.s. MWNT

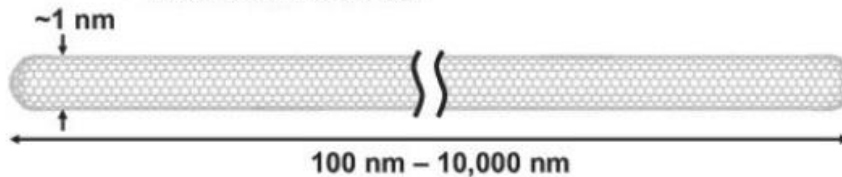
## SWNT

SWNTs are unique:

- Molecules
- Perfect structures
- Polymers of pure carbon

SWNTs have extraordinary properties:

- Strength (~100x steel)
- Electrical conductivity (~ copper)
- Thermal conductivity (3x diamond)
- Accessible surface

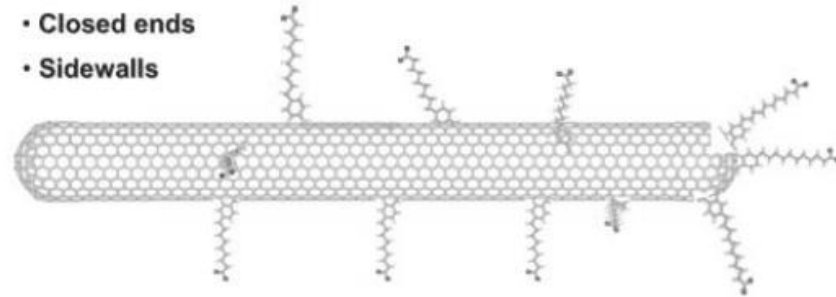


**Figure 2.24** SWNTs are the perfect material with unique and extraordinary properties. (Courtesy of CNL)

In most applications, raw SWNTs will need to be customized

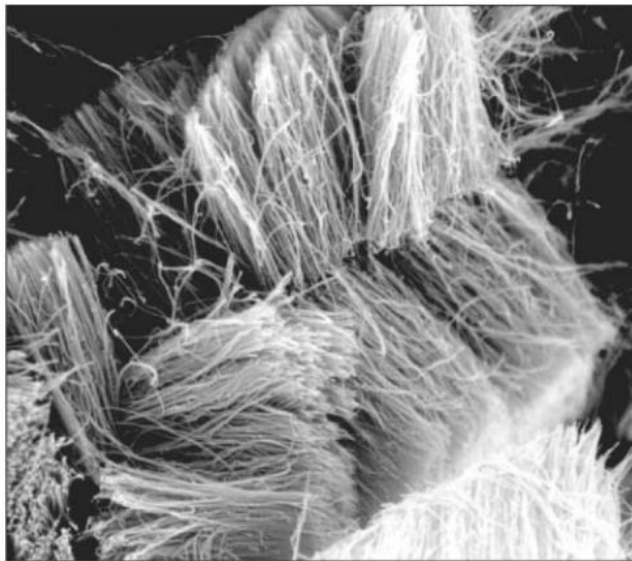
This customization can be precisely controlled using everyday organic chemistry

- Open ends
- Closed ends
- Sidewalls

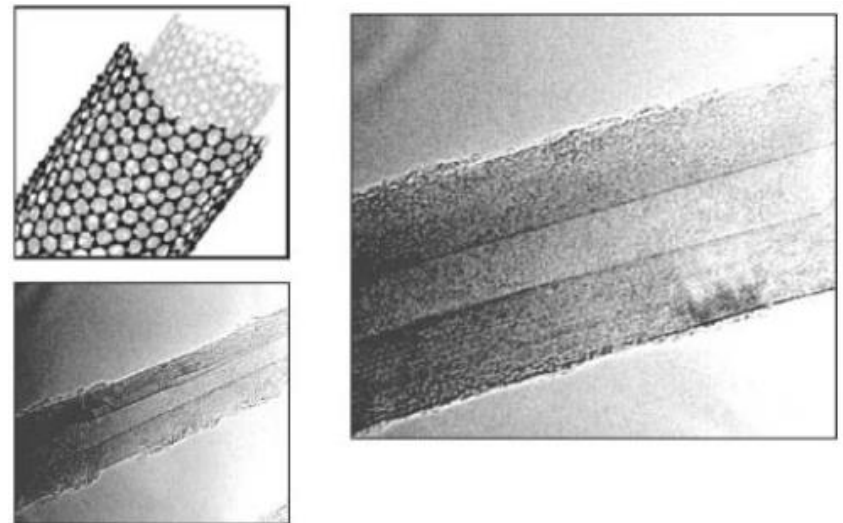


**Figure 2.25** SWNTs can be customized and controlled using organic chemistry. (Courtesy of CNL)

## MWNT



**Figure 2.29** MWNTs have dimensions of 2 to 10 nm ID, 20 to 75 nm OD, and are 50  $\mu\text{m}$  long.



**Figure 2.31** Microstructures of MWNTs in cartoon and TEM micrographs.

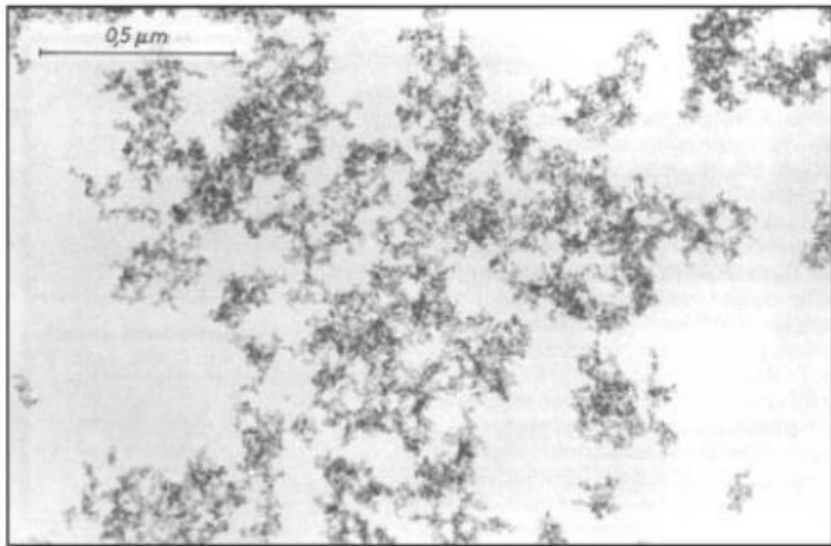
## 7.7.4 Nanosilica

- Origin

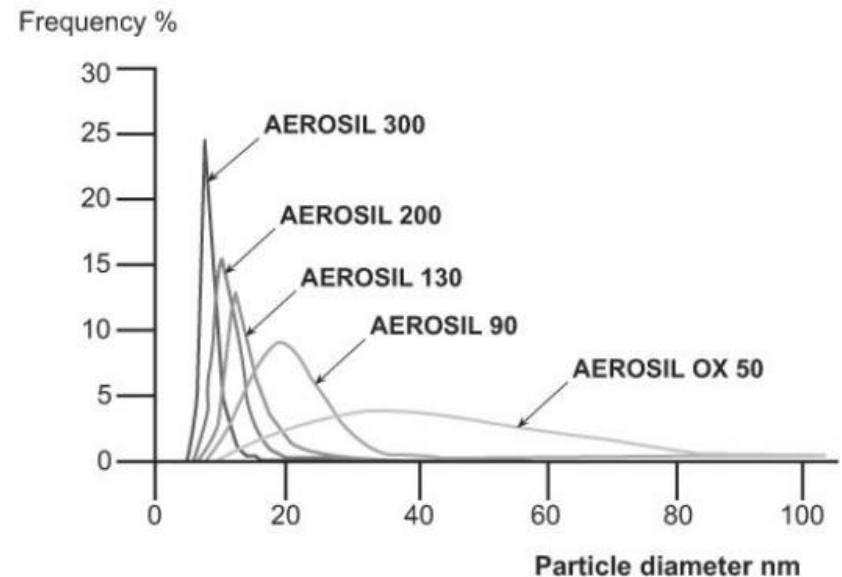
- In 1941, nanosilica was produced by a high temperature hydrolysis process of metallic oxides
- Silicon dioxide, aluminum oxide, titanium dioxide

- Properties

- highly dispersed, amorphous, spherical, and free of pore
- easy to aggregate due to high surface area
- used to adjust the rheological properties of epoxy resins (**thickening agent**)



**Figure 2.33** TEM micrograph of AEROSIL 300 showing particles in aggregates. (Courtesy of Degussa.)

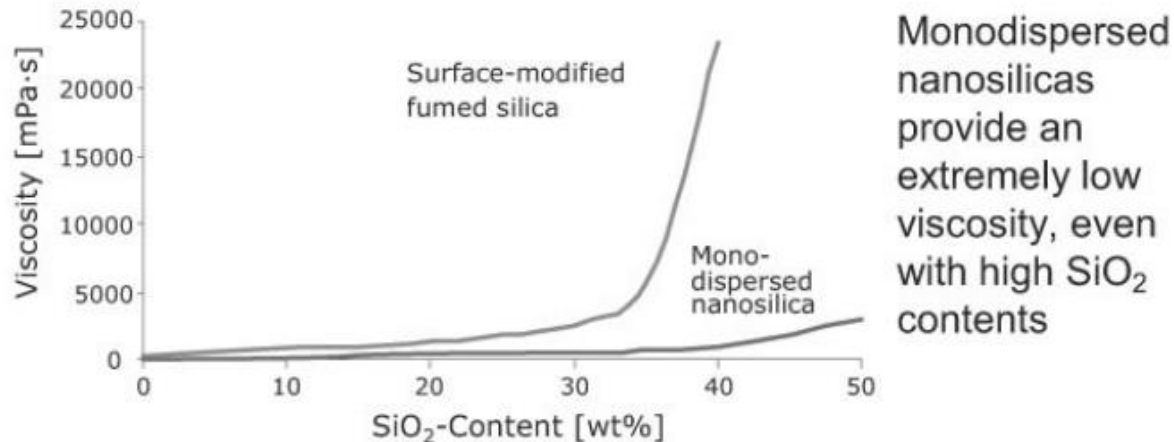


**Figure 2.34** Particle size distributions of various grades of AEROSIL nanosilicas. (Courtesy of Degussa.)

- Properties

- Nanosilica nanocomposites have these enhanced properties:

- Enhanced scratch, abrasion resistance, and transparent products
- Unique toughness and stiffness
- Reduced thermal yellowing (황변), thermal expansion
- Improved electrical insulation



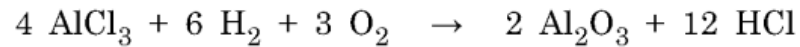
**Figure 2.38** Viscosities of fumed silica and monodispersed nanosilica in acrylate ester. (Courtesy of Hanse Chemie.)

## 7.7.5 Nanoaluminium oxide

- Properties

- The formation of the highly dispersed oxides is :

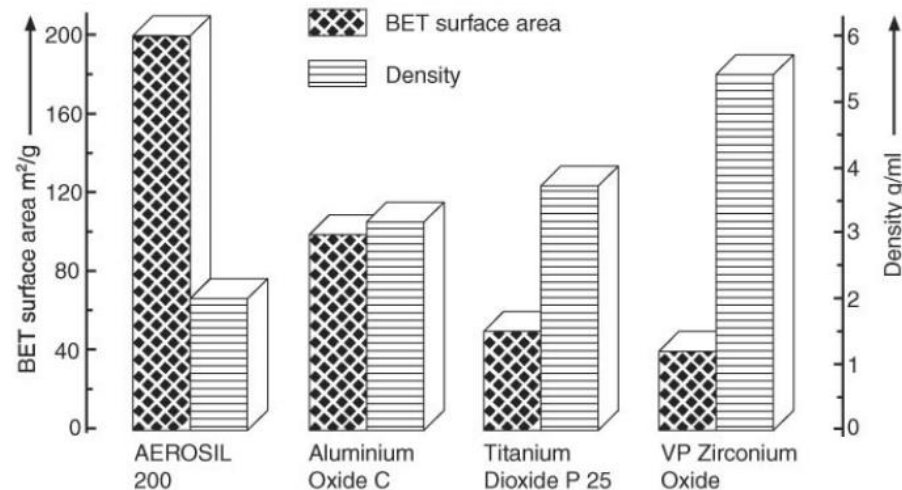
Aluminum Oxide C



Titanium Dioxide P 25



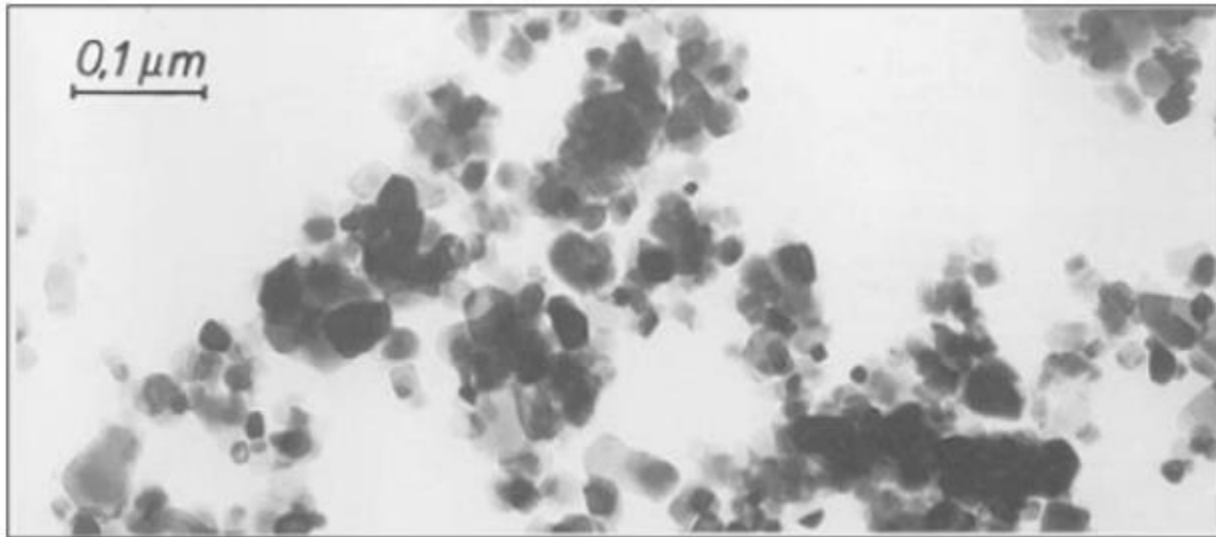
- Aluminum oxide has an average particle size of about 13 nm
    - applications : production of aluminum nitride, ink-jet papers, thermo-transfer printing, cable insulation, high voltage insulator, transparent coatings, solder-resistant mask, heat insulation mixtures, improved stereo-lithographs



**Figure 2.40** Comparison of BET surface areas and densities of AEROSIL 200,  $\text{Al}_2\text{O}_3$  C,  $\text{TiO}_2$  P 25, and  $\text{ZrO}_2$ . (Courtesy of Degussa.)

## 7.7.6 Nanotitanium oxide (TiO<sub>2</sub>)

- Properties
  - Excellent additive to improve the [heat stability of silicone adhesive/sealant](#)
  - Flame retardancy to silicone using only a small amount of nanotitanium oxide
  - applications : high-voltage insulation material, toner, battery separators, etc.



**Figure 2.42** TEM micrograph of Titanium Dioxide P 25. (*Courtesy of Degussa.*)



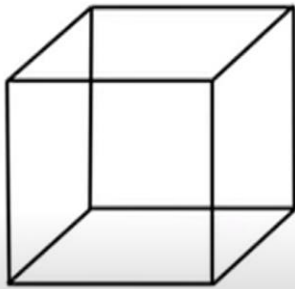
## 7.8 Polyhedral oligometric silsesquioxane (POSS)

- Origin

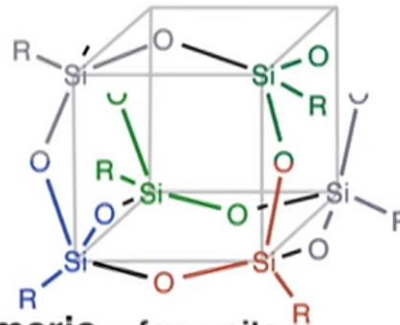
- Inorganic building blocks are incorporated into organic polymers.
- POSS as multifunctional polymer additives  
: molecular level reinforcements, processing aids, and flame retardants.

- Properties

- Two unique structural features :
  - (a) chemical composition is a hybrid, intermediate w/t silica ( $\text{SiO}_2$ ) and silicones ( $\text{R}_2\text{SiO}$ )
  - (b) POSS molecules are nanoscopic in size, ranging from approximately 1 to 3 nm.
- Hybrid materials :
  - tough, lightweight and as easy to process as polymers (polymer properties)
  - thermal resistance and oxidation resistance (Ceramic properties)



**Polyhedral** = many-sided 3-D shape



**Oligomeric** = few units  
**Silsesquioxane** =  $(\text{RSiO}_{1.5})_n$

- Features

- Unlike silica or modified clays, POSS molecule contains covalently bonded reactive functionalities suitable for polymerization or grafting POSS monomers to polymer chains.
- Each POSS molecule contains non-reactive organic functionalities for solubility and compatibility of the POSS segments with the various polymer systems.
- POSS is soluble in most common solvents, resins and monomers, and can be used as common organic additives to nearly all polymer types.

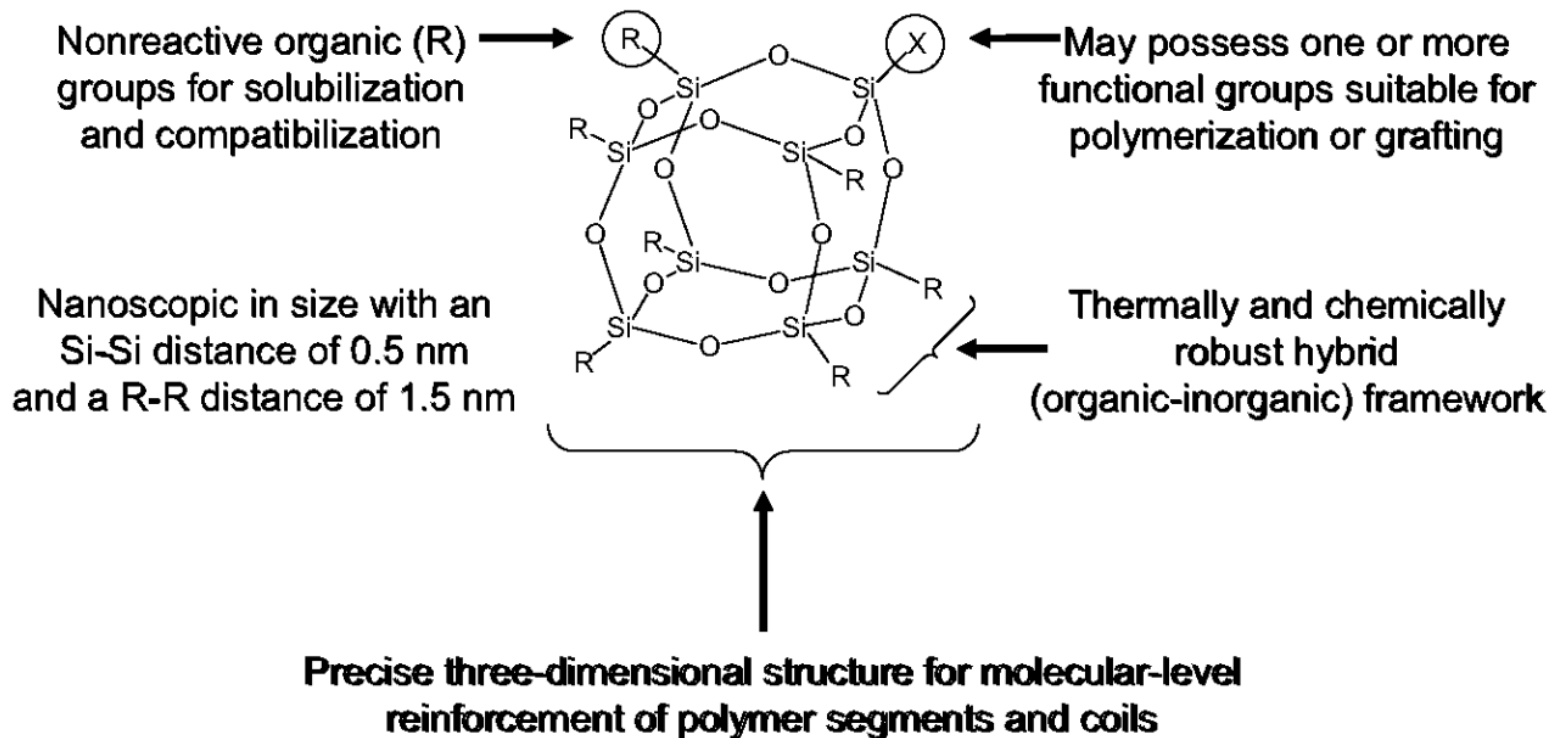


Figure 2.16 Anatomy of a POSS molecule. (Courtesy of Hybrid Plastics.)



- Features

- Inorganic building blocks are incorporated into organic polymers.
- POSS nanostructured materials can be used as multifunctional polymer additives acting simultaneously as **molecular level reinforcements, processing aids, and flame retardants**.

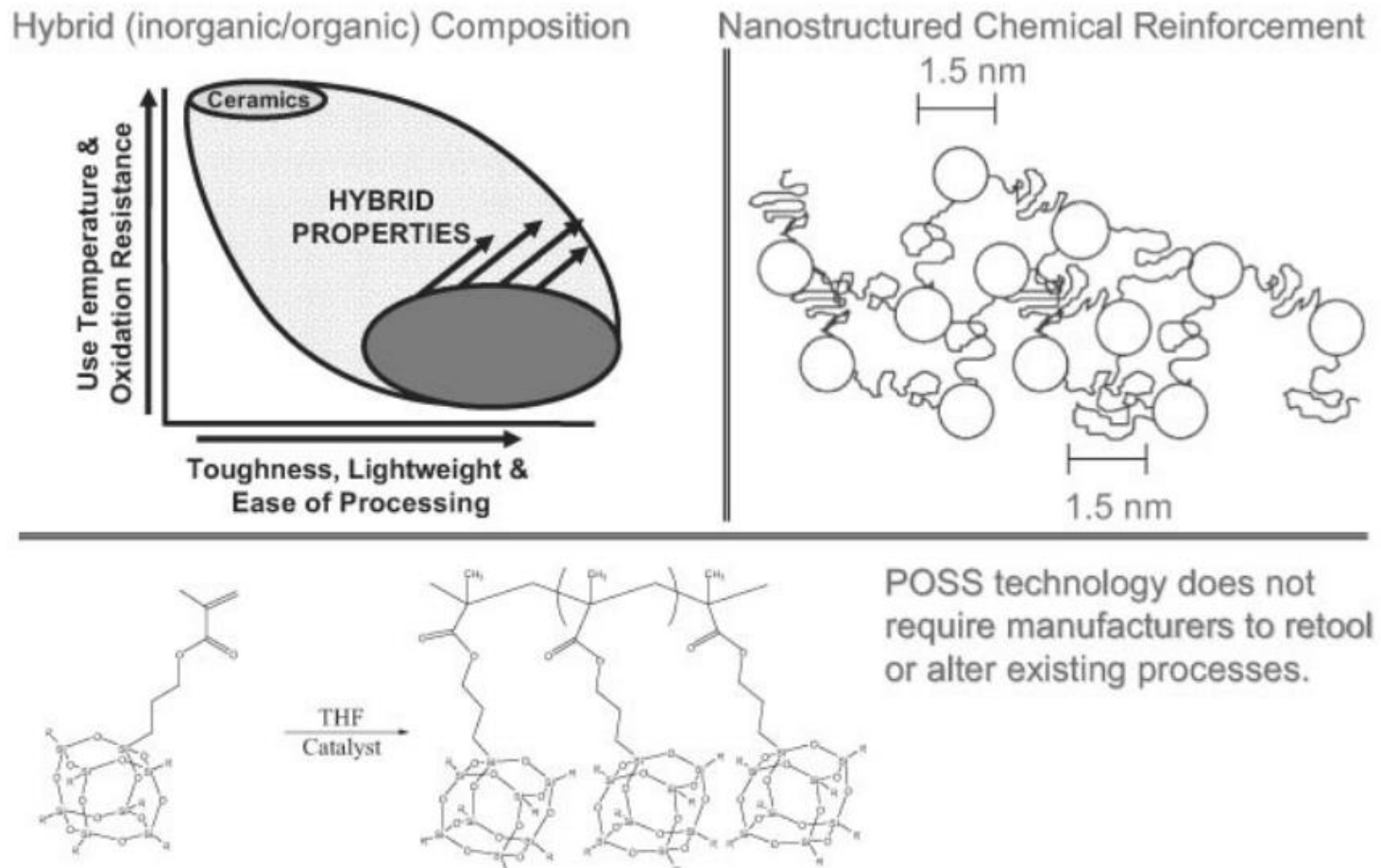
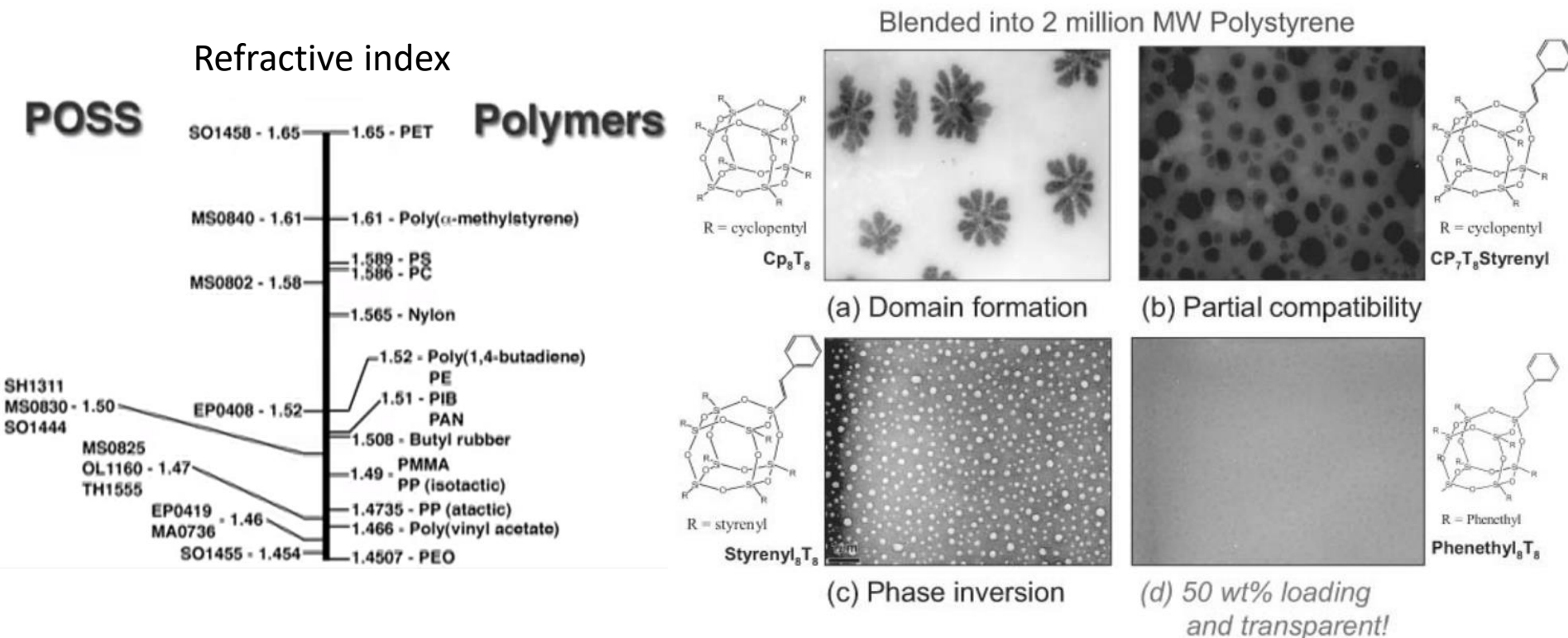


Figure 2.18 Key aspects of POSS technology. (Courtesy of Hybrid Plastics.)

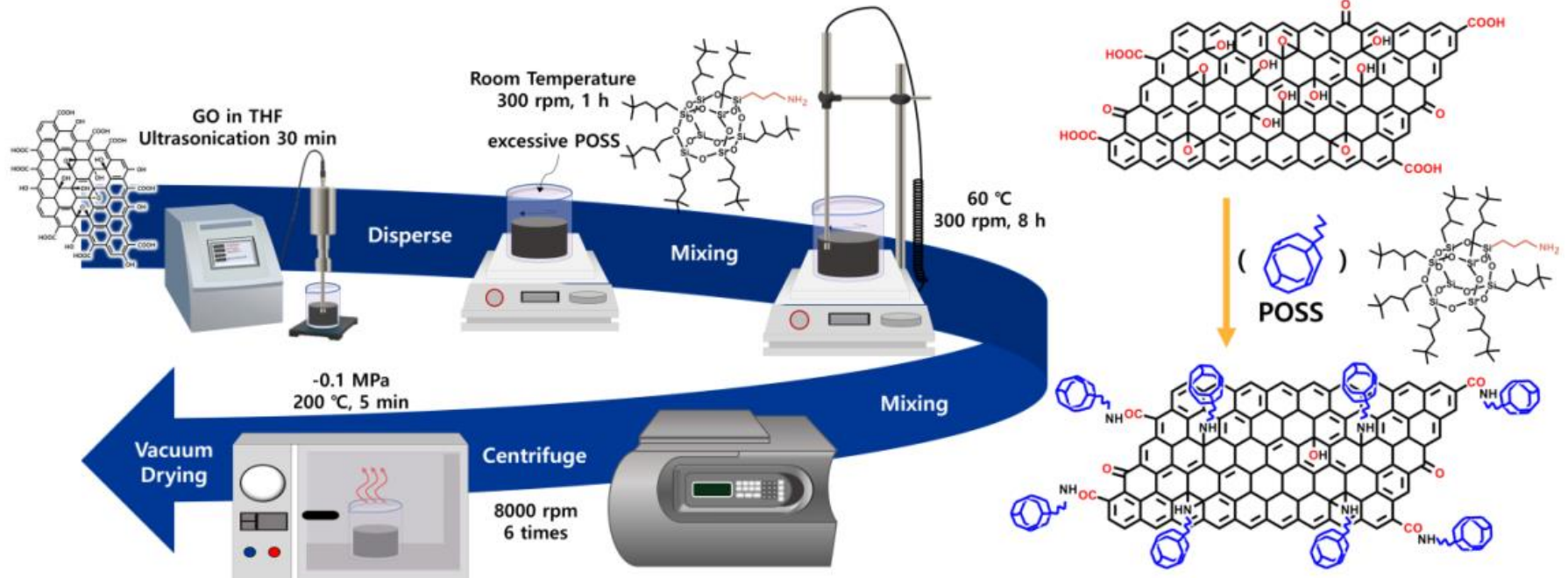
## • Features

- It is important to match RI while making polymer blends with nanomaterials for transparent optical properties.
- By **changing - R groups on POSS**, RI can be within the ranges of various polymer materials
- When POSS is melt blended with polymers, it may phase-separate (Opaque and hazy composites).
- As the POSS molecule becomes more compatible with polymer matrix, the POSS domain becomes smaller and completely dispersed (clear and transparent composites)



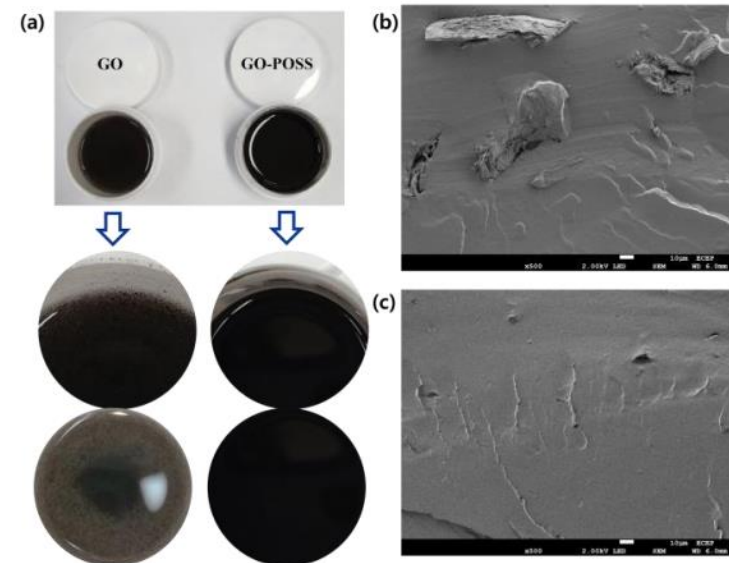
**Figure 2.21** TEM micrographs showing the change of morphologies of polystyrene by changing the R group of the POSS materials. (Courtesy of A. Lee.)

- GO-POSS dispersion in polymer matrix



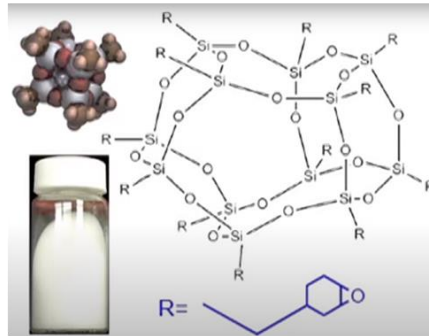
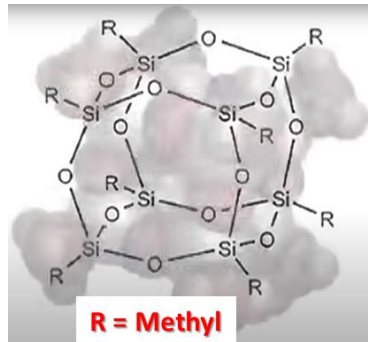
- R-group in POSS is functionalized by GO, resulting in good chemical bonding.

- POSS-functionalized GO shows better dispersibility and less filler aggregation in the polymer matrix.

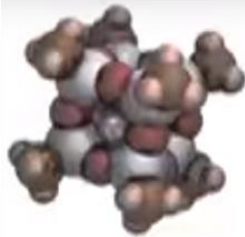


## • Features

- Depending on -R groups on POSS, the density and physical properties may vary.
- Through condensation or addition reactions, copolymerization and crosslinking with other polymers can easily be achieved.



<b>Density</b>	
Material	Density (g/cm <sup>3</sup> )
Amorphous silica	2.18
SH1311 (octahydro)	1.82
MS0822 (octaethyl)	1.33
MS0805 (octaisooctyl)	1.01
Iso-octane	0.69



Solid (white powder)



Semi-solid (Grease)



Viscous liquid



# Ch. 8. Processing of nanomaterials

## 8.1. Synthesis methods

- After the selection of a polymer matrix and appropriate nanoparticles, the next challenge is to determine the proper synthesis method to create desired polymer nanocomposites.

### Challenge

#### Age-old Blend Questions:

- Process from Agglomerate to Dispersion: Activation Energy?
- Final Dispersion: Thermodynamic vs. Kinetic Stability?

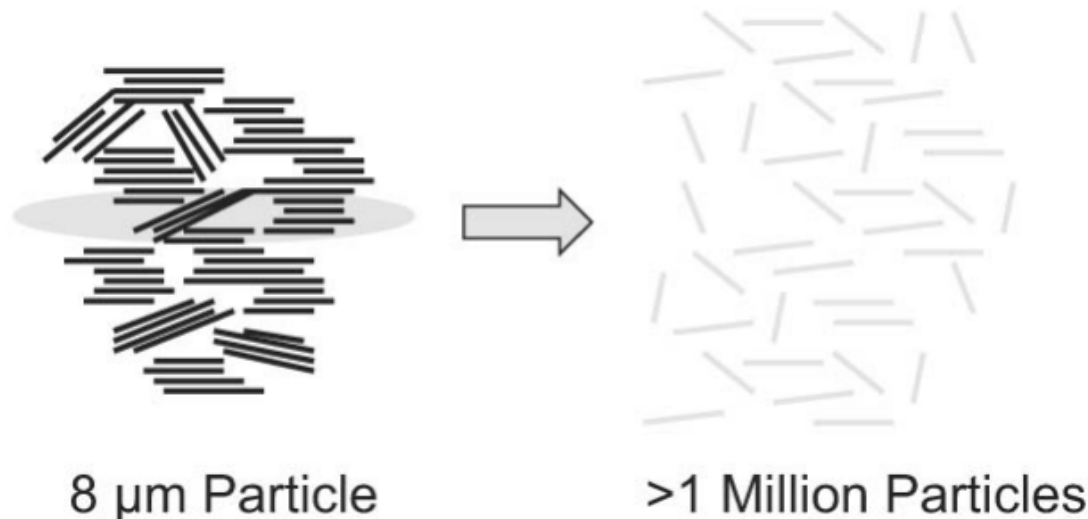


Figure 4.1 Processing challenge of layered silicate. (Courtesy of SCP.)



## 8.1. Synthesis methods

- For **solid thermosetting** reactive pre-polymers or thermoplastic polymers with nanoparticles, the following processing methods are recommended:

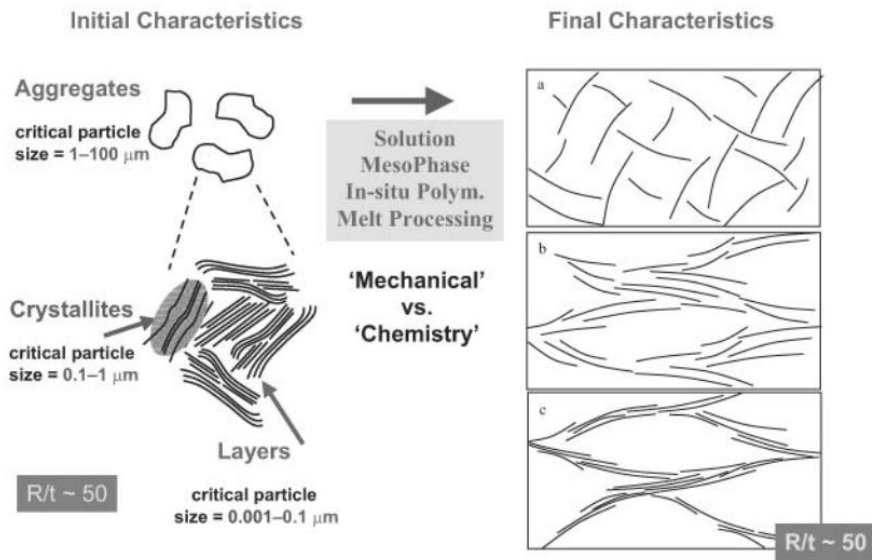
- Solution intercalation
- Melt intercalation
- Roll milling

- For **liquid thermosetting** reactive pre-polymers or thermoplastic polymers with nanoparticles, the following processing methods are recommended:

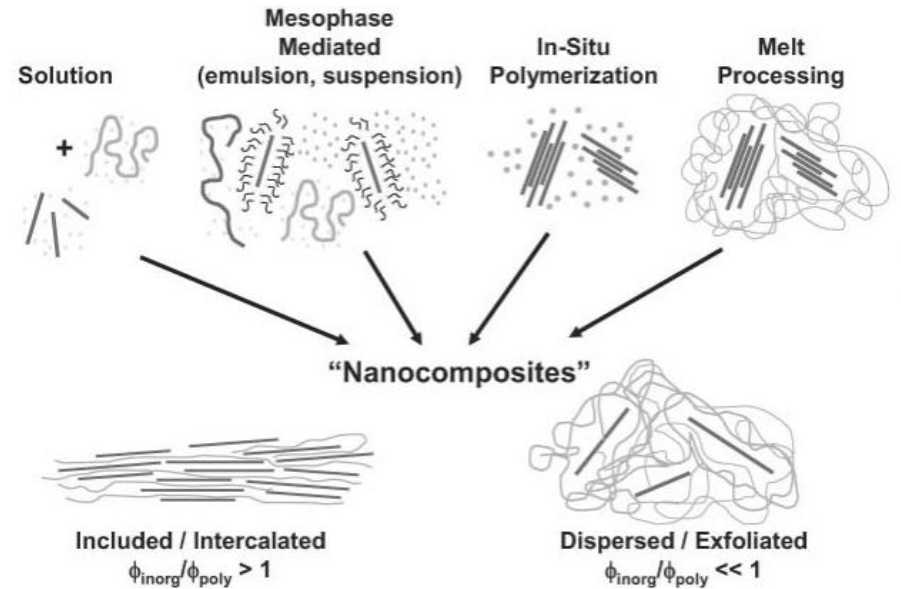
- In-situ polymerization
- Emulsion polymerization
- High-shear mixing

- Real challenge : suitably disperse the chosen polymer into the aggregated or layered nanoparticles.
- Solution intercalation, mesophase (emulsion or suspension), in-situ polymerization, and melt processing are convenient methods to disperse layered silicates into nanocomposites

### Challenge: Dispersion



**Figure 4.2** Dispersion of layered silicates using different processing methods. (Courtesy of R. Vaia.)



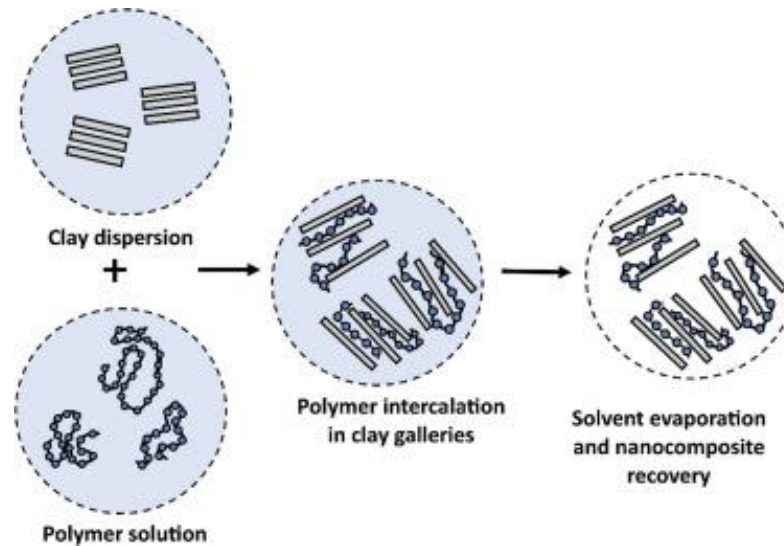
**Figure 4.3** Various synthesis methods to disperse layered silicate into nanocomposites. (Courtesy of R. Vaia.)

- Optimum mechanical properties of the nanocomposite are obtained when the **layered silicate is fully exfoliated with polymer**.
- **Intercalation of layered silicate with polymer** enhances mechanical properties **but not as optimum as exfoliated systems**.

## 8.2. Solution intercalation

- The layered silicate is exfoliated into single layers using a solvent in which **the polymer or pre-polymer is soluble**.
- Clay layers are firstly swollen or dispersed in the solvent, followed by the addition of the dissolved polymer into the clay solution.

Ref) Med. Chem. 6 (2016) 201-210

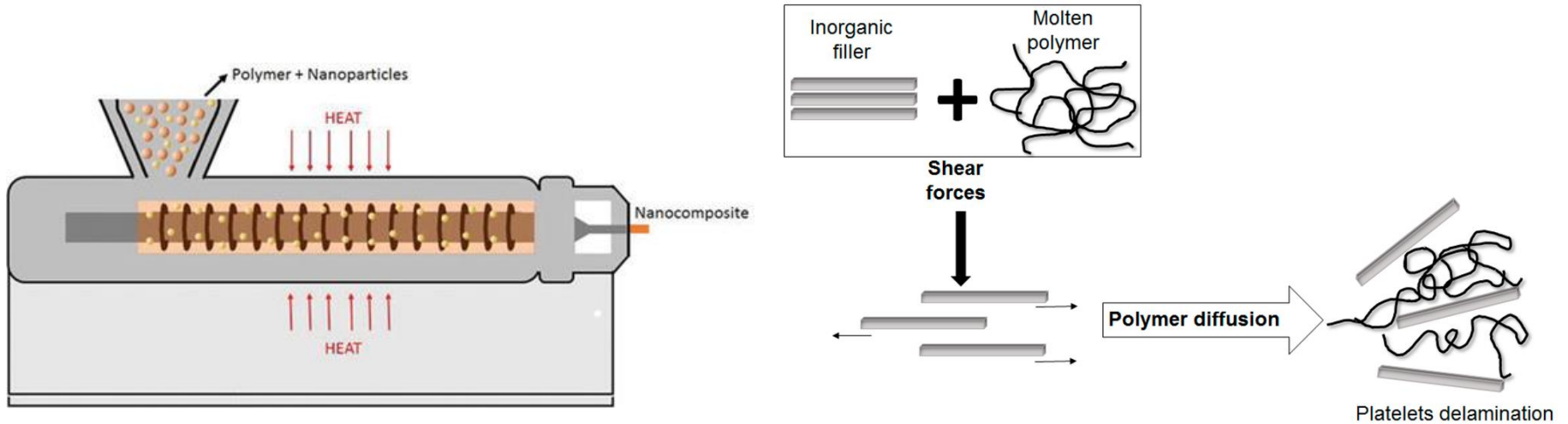


- Advantage
  - The low viscosity of the solution : easy particle dispersion
  - Water-soluble polymers can be used for this technique
  - Easy processing



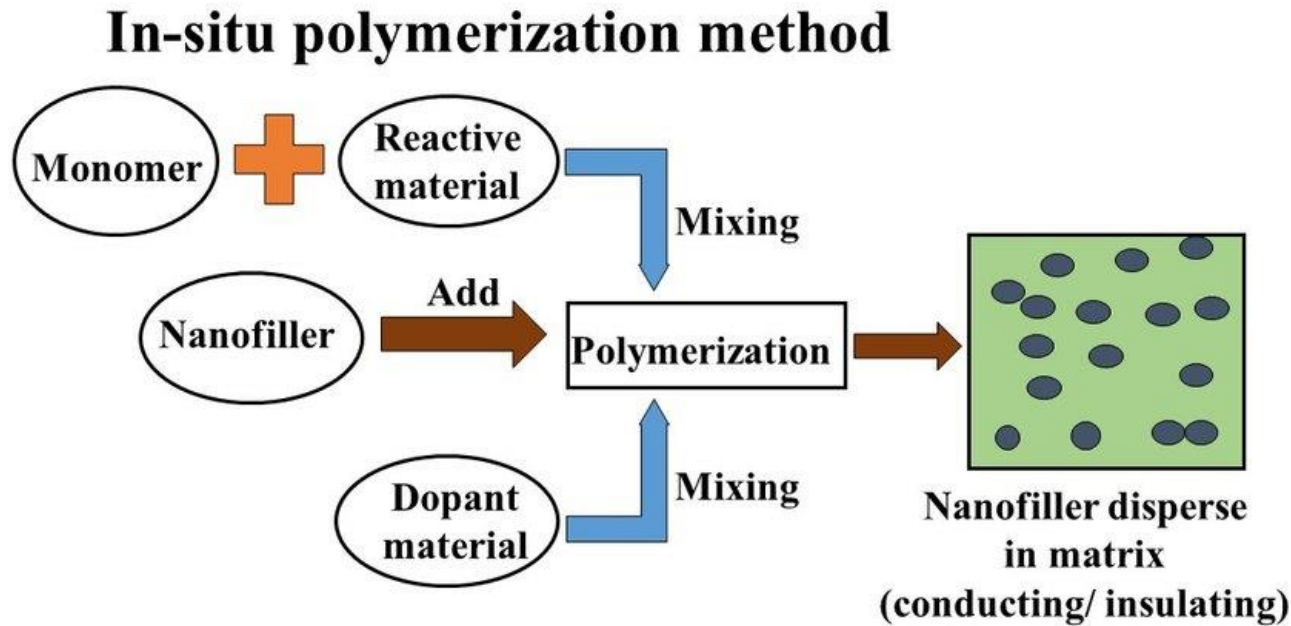
## 8.3. Melt intercalation

- The layered silicate is mixed with the solid polymer matrix **in the molten state**.
- No solvent is required



## 8.4. In-situ polymerization

- Polymerization can occur between the intercalated sheets.
- Polymerization can be initiated by different methods such as heat or radiation, diffusion of a initiator, organic initiator or catalyst.
- Involve **a chemical reaction** resulting in the formation of **very fine and thermodynamically stable reinforcing phase within a matrix**.



- e.g. : Fabrication of polymer/clay nanocomposites

