IEEE CEIDP 2012
Workshop on Nanodielectrics

Processing of nanocomposites

Davide Fabiani – University of Bologna
Edward A. Cherney – University of Waterloo
Isaias Ramirez Vazquez – Insituto de Investigaciones Electricas
Thomas Andritsch – Delft University of Technology

DEIS Technical Committee on Nanodielectrics

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- Surface treatment
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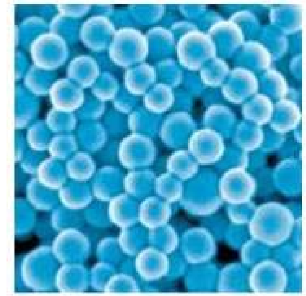
- Effect of synthesis method
- Effect of contaminants

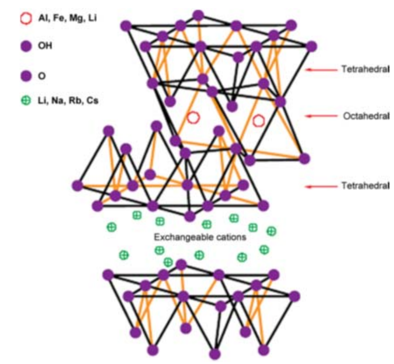
Nanofillers

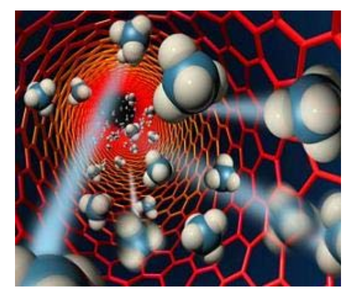
- Nanofillers:
  - Different kinds of nanofillers:
    - (quasi)-spherical particles
    - whiskers and rod particles
    - platelet (lamellar) particles

    ↓ increasing aspect ratio

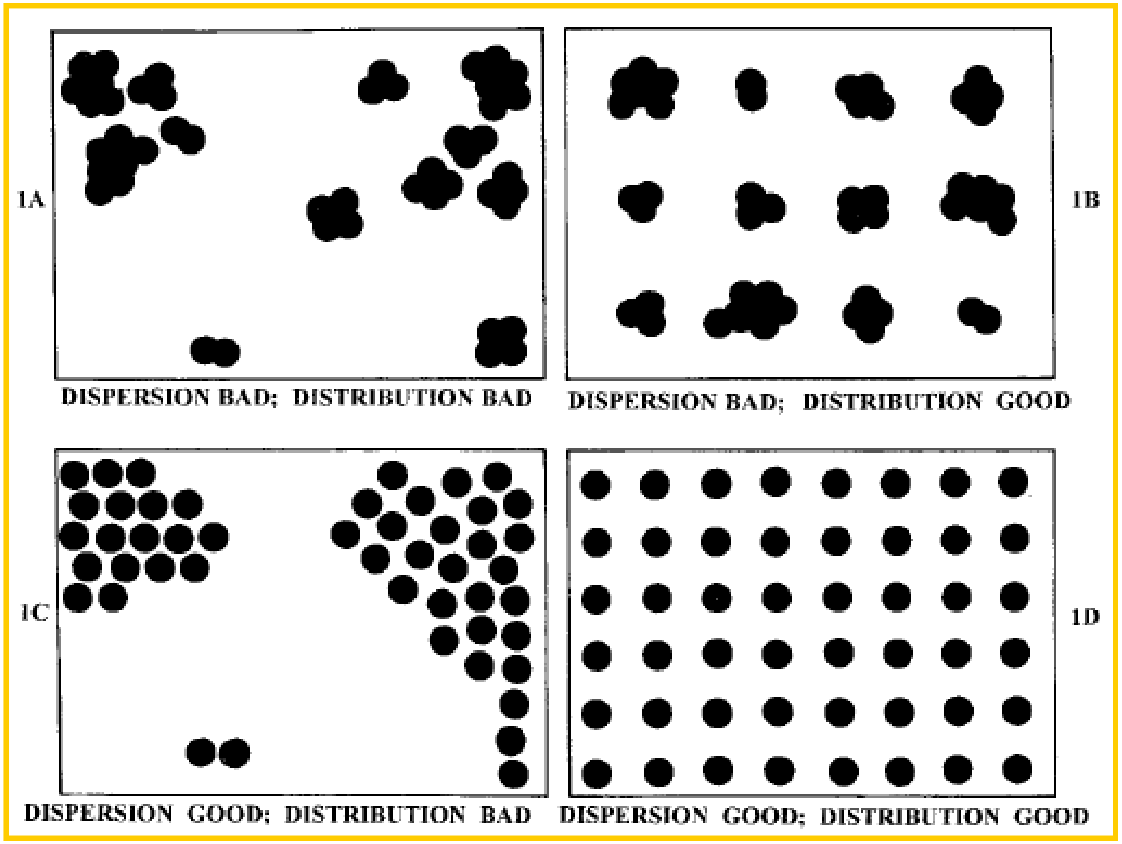
  - Four main groups, such as:
    - silicon oxides (silica)
    - metallic oxides and hydroxydes (alumina, titanium oxide, magnesium oxide, zinc oxide, boehmite, hydrotalcites, etc.)
    - nanoclays (montmorillonite, hectorite, etc.)
    - carbon nanotubes, fullerenes







The problem with nanofillers...



Aims of nanocomposite processing

- Even dispersion and distribution of nanoparticles in the host material
  - Nanocomposites show their remarkable properties only when particles are well distributed in the host material
  - Nanofillers usually incompatible with polymers used in electrical engineering

- Reliable results

Surface treatment

- E.g.: unmodified silica → silanol groups on particle surface → hydrophilic. Surface hydroxyls increase the tendency to create hydrogen bonds between nanoparticles, thus directly result in the formation of aggregates
- Possible solution: use of surfactants

- Surfactants have two parts, hydrophilic and hydrophobic chain segments combined in the same molecule
- A surfactant lowers the surface energy of the filler and the interfacial tension between the particles and the matrix, thereby facilitating the separation and improvement in the dispersion of the particles during mixing.

Silanization

- A multitude of silane coupling agents are available
- Common formula:

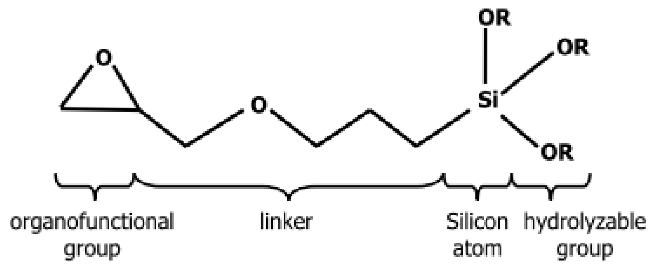
$$R(CH_2)_nSi\,X_3$$

X ... hydrolysable group

R ... functional group compatible with host

- Example: 3-(2,3-epoxypropoxy)propyltrimethoxysilane

Reacts with epoxy resin ←

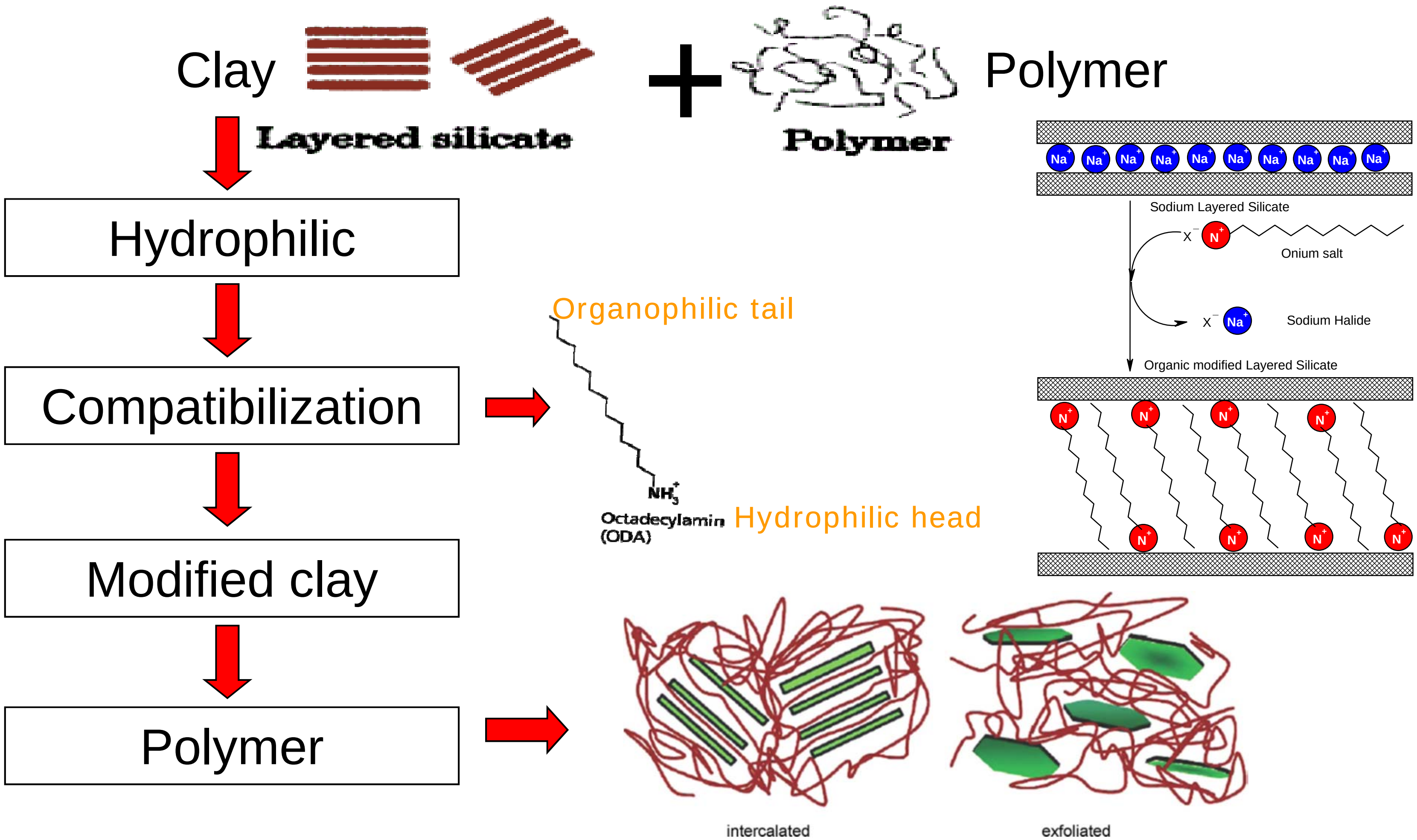


→ Reacts with particle surface

- Silane coupling agent has to be chosen according to host polymer and particle surface

Surface treatment

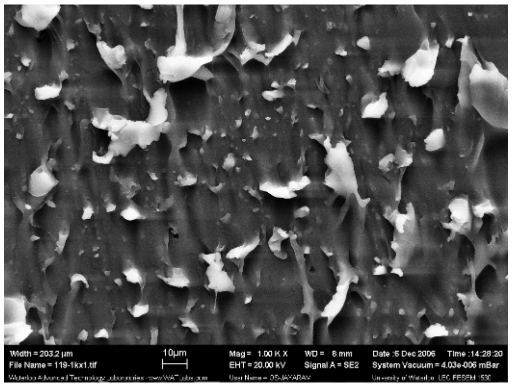
⌘ Organic modification (clays..)

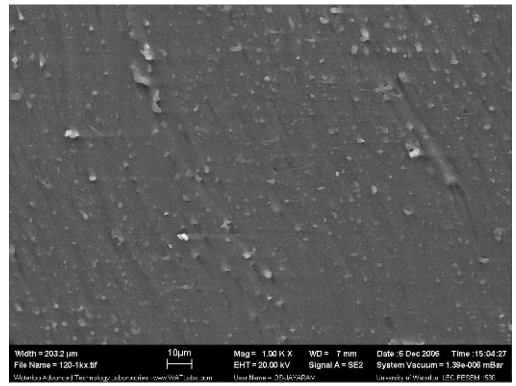


Effect of surface treatment

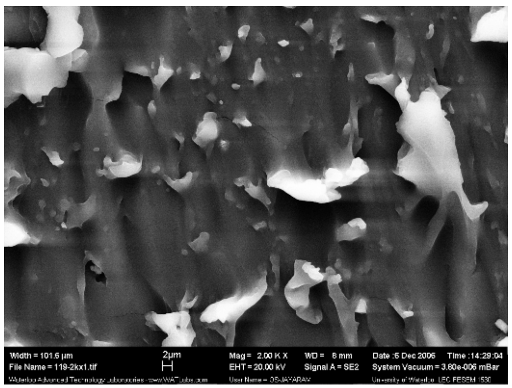
Effect of Triton in composites containing 2.5% by weight nano Al_2O_3 + 97.5% SiR

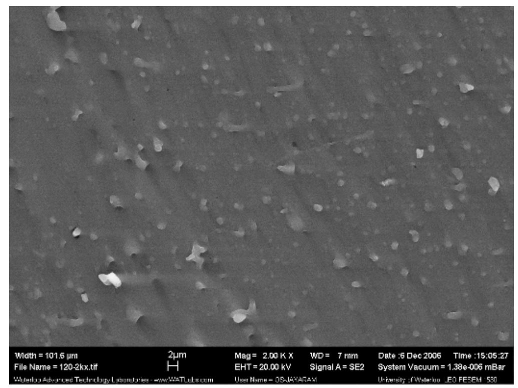
(left column without surfactant; right column with surfactant)





Magnification 1000 x





Magnification 2000 x

Processing of Nanocomposites

Common methods:

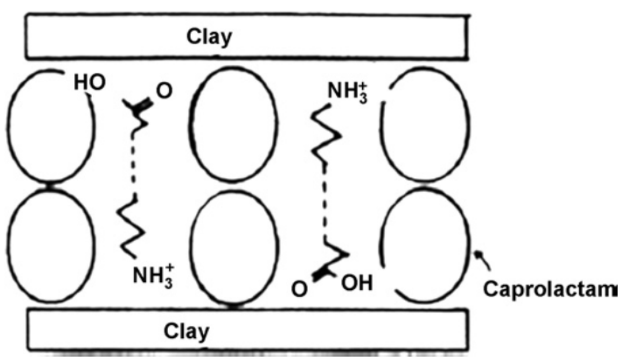
- In situ-polymerization
- Solvent-method
- Melt blending
- Sol-gel
- Electrospinning

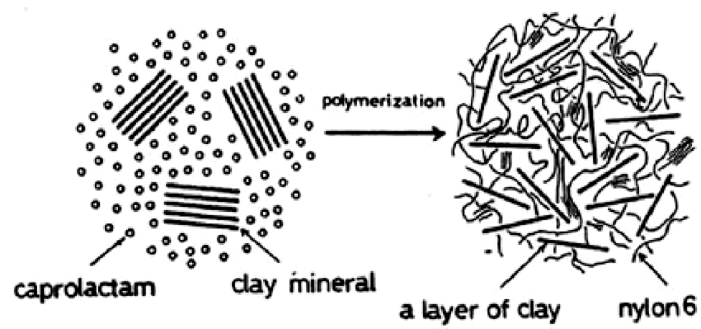
In situ polymerization

Thermoplastic polymers

⌘ First successful attempts to obtain thermoplastic NC modifying montmorillonite (MMT)

⌘ Swelling of the monomer (caprolactam) and clay → polymerization





Schematic illustration for synthesis of Nylon-6/clay nanocomposite

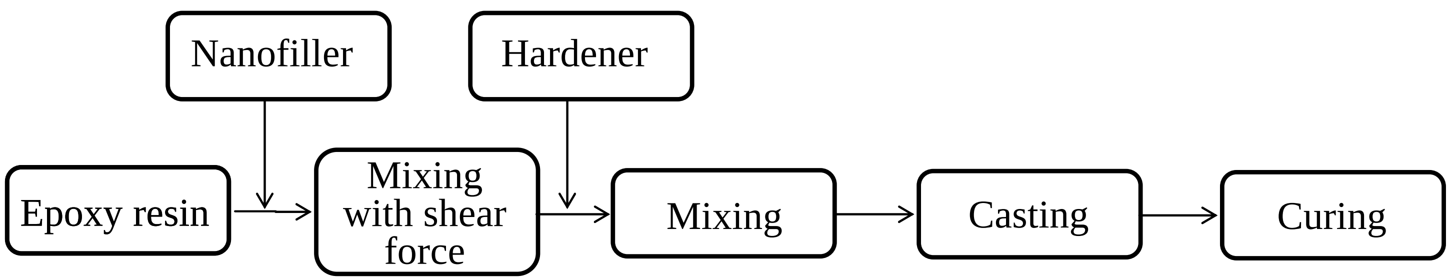
⌘ Different kinds of thermoplastic polymer matrix can be used, such as polyolefins (PP, PE, EVA), PET, PMMA, PS, etc.

In situ polymerization

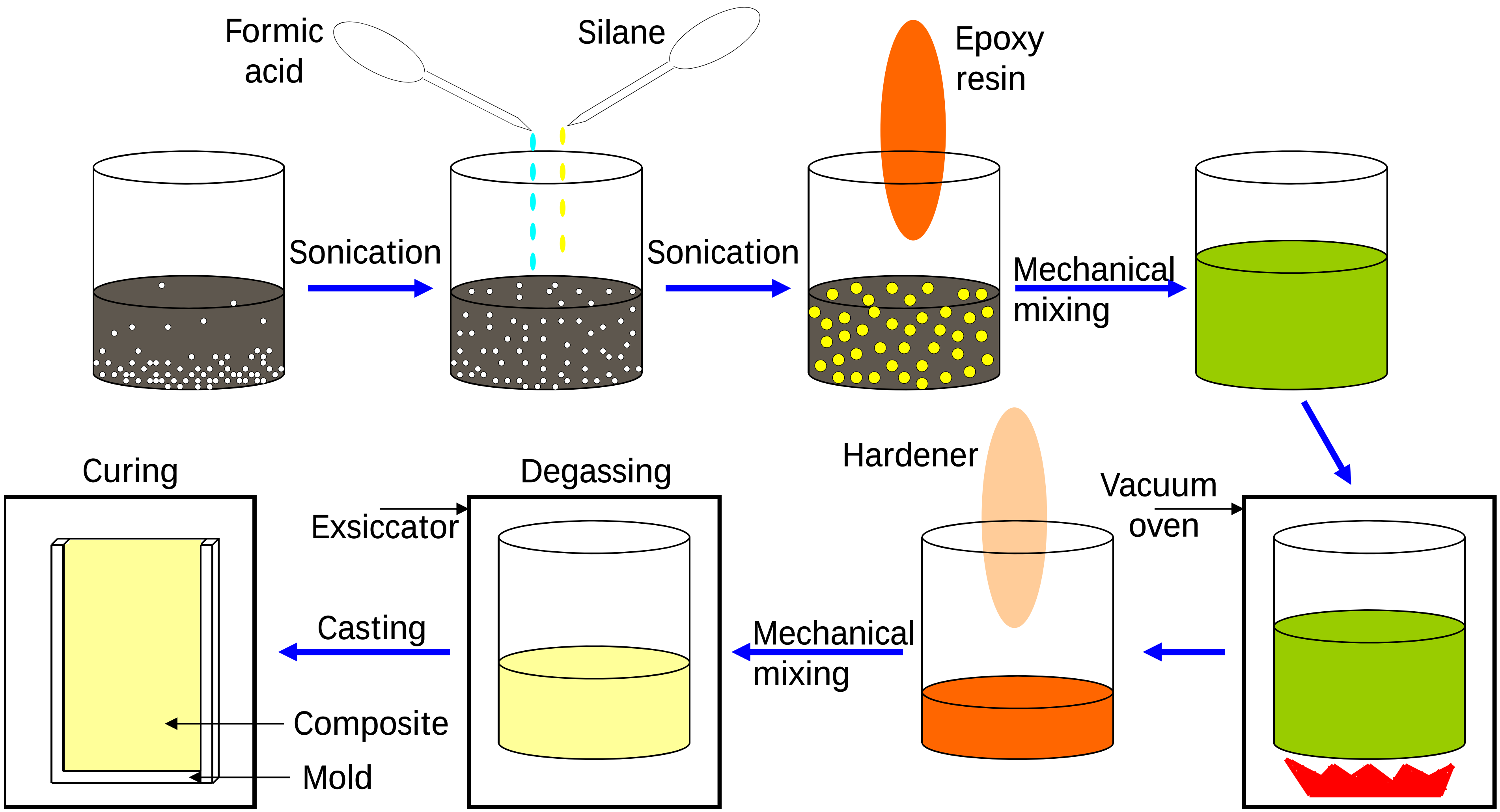
Thermosetting polymers

⌘ In-situ polymerization is the main technique for the preparation of thermosetting NC, which cannot be synthesized by melt blending

⌘ In the case of organoclays used as nanofillers, both exfoliated and intercalated NC can be obtained

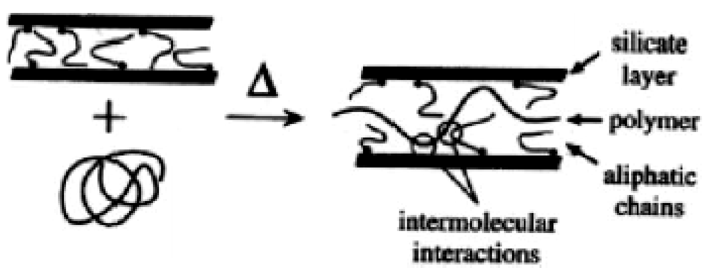


Example for synthesis



Melt blending

- Extrusion melt compounding of dispersive nanofillers with polymeric materials
- Effective and economical process
- Major advantage: allows NC to be formulated using ordinary compounding devices: extruders or special mixers, without the necessity of using advanced polymer technology.
- Mixing parameters strongly affect the polymeric NC morphology
- Only thermoplastic polymers



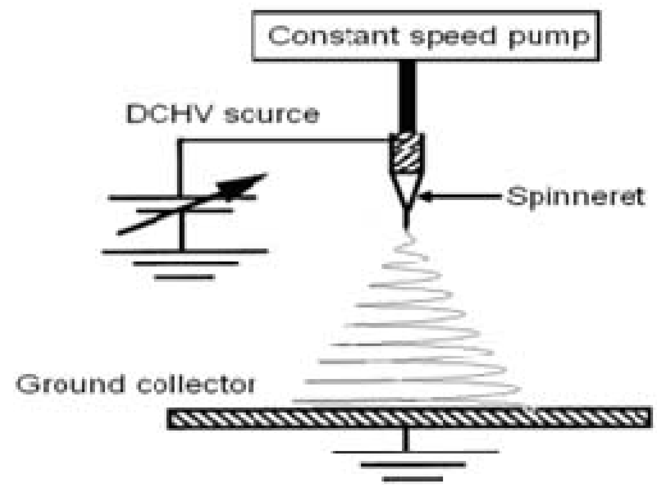
Schematic depicting the intercalation process between a polymer melt and an OMLS

Melt blending

- Major variables to take in account are:
  - proper balance of **distributive** and **dispersing** mixing and, in turn,
  - design of screw, specifically length and position of mixing zone,
  - melt temperature,
  - residence time of melt,
  - shear and elongational forces...
- Complete dispersion of nanoparticles can still be difficult

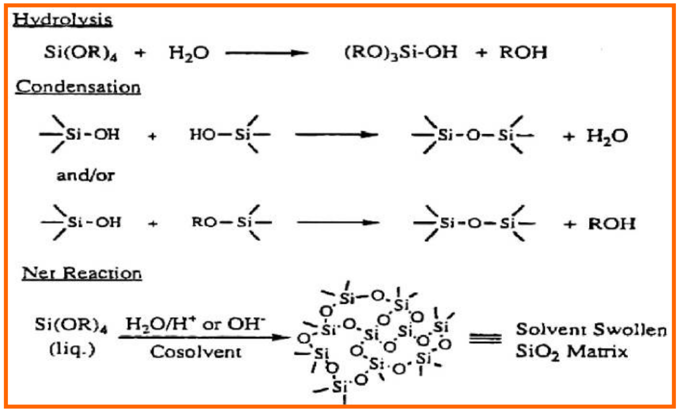
Electrospinning (example)

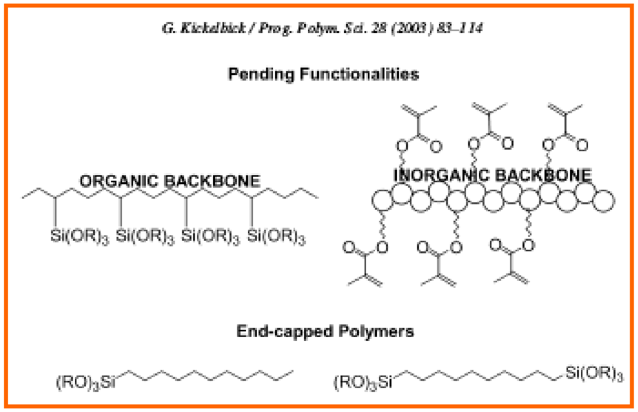
- Fumed silica mixed with ethanol using a magnetic stirrer to wet silica
- Wetted fumed silica mixed with part A with high shear mixer
- Mixture electrospun producing filaments of Part A with nano fumed silica
- Part B added to filaments of Part A containing nano fumed silica and mixed at low speed
- Mixture degassed, poured into molds & cured

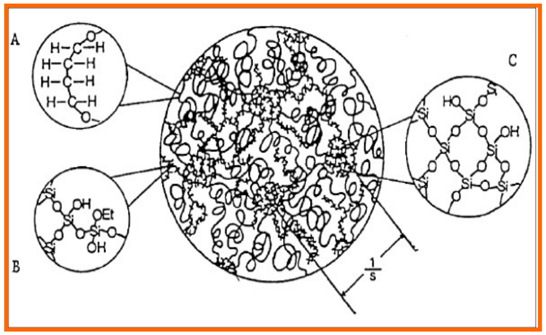


Sol-gel process

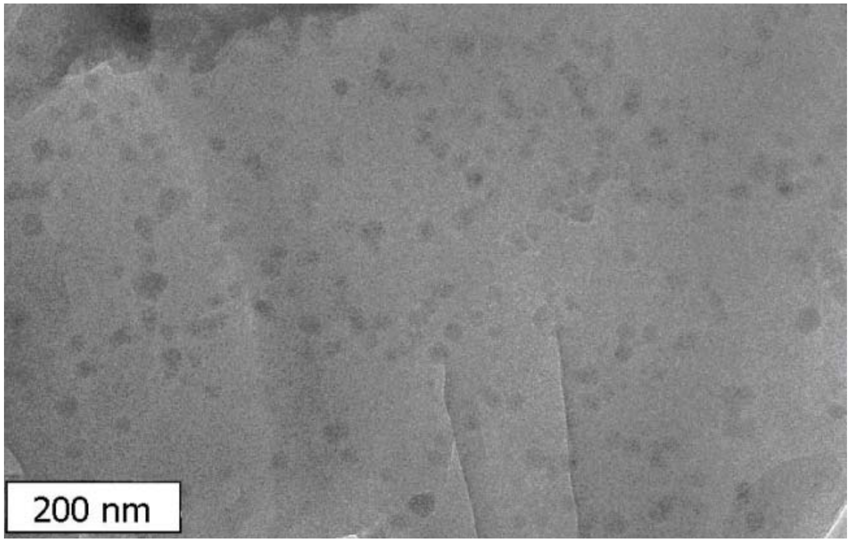
- The sol-gel method is widely used in the preparation processes for inorganic/organic NC.
- It consists of hydrolysis of the constituent molecular precursors and subsequent polycondensation to glass-like form
- Organic polymers can be introduced at the initial stage, in which the nanoparticle of sol can remain homogeneously dispersed at nanometric scale.



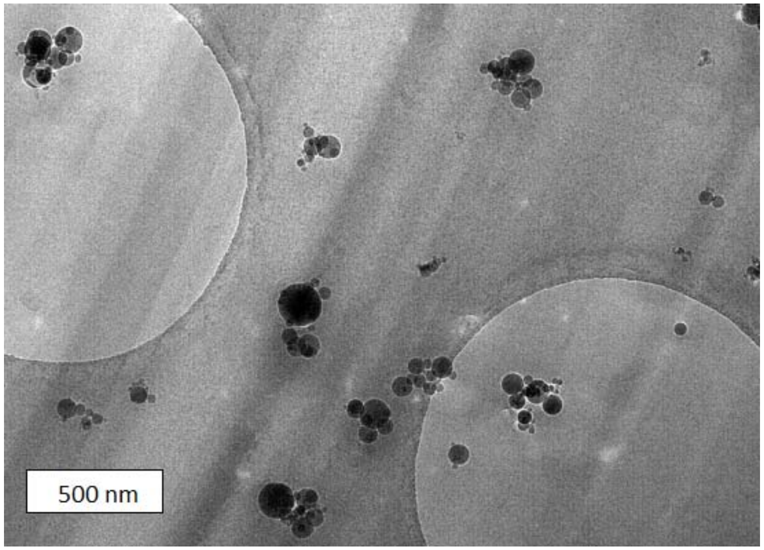




Sol-gel process



Typical particle distribution
sol-gel process



Typical particle distribution
in-situ polymerization

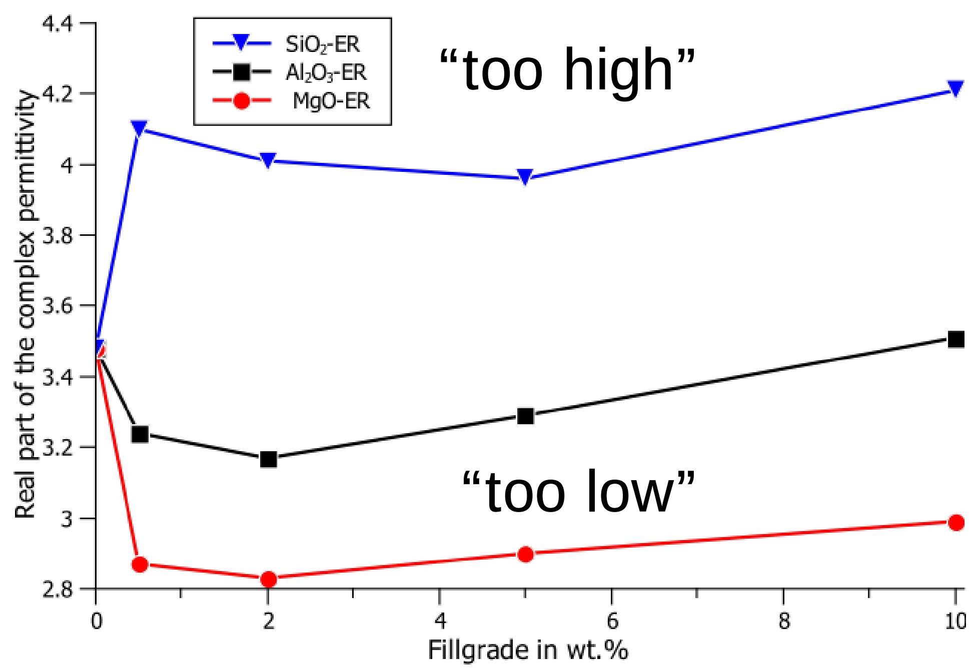
Effect of synthesis method

- Permittivity of SiO_2-epoxy with sol-gel method compared to Al_2O_3 and MgO-epoxy with in-situ method

Permittivities:

- Base resin: ~3.5
- Silica: ~4
- Alumina, MgO ~10

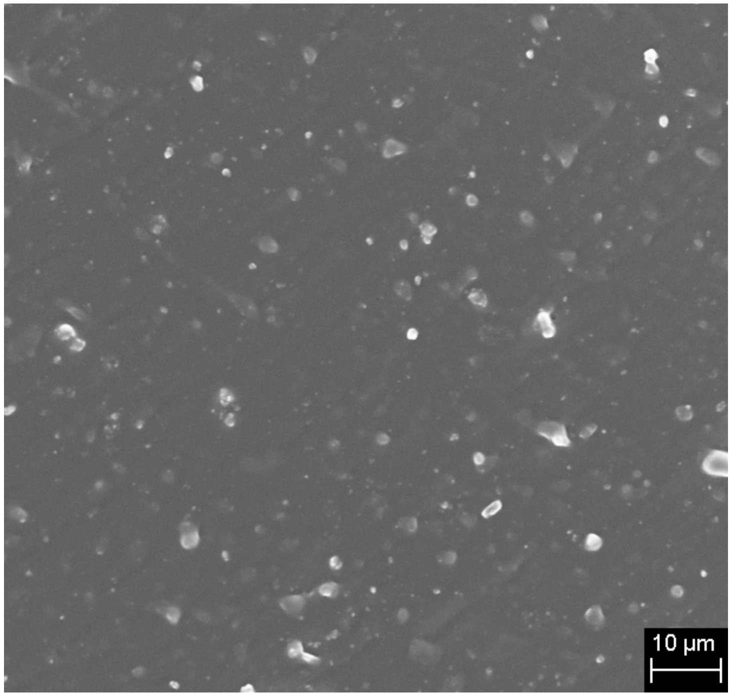
- Synthesis method has impact on dielectric properties



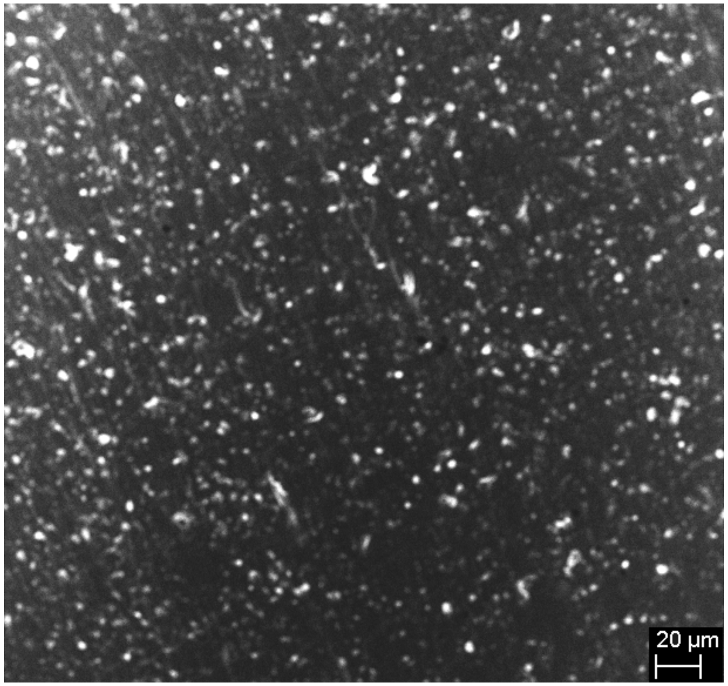
Effect of synthesis method

Comparison of particle dispersion and distribution for samples prepared with electrospinning compared to mechanical mixing

6 wt% silica in silicone rubber



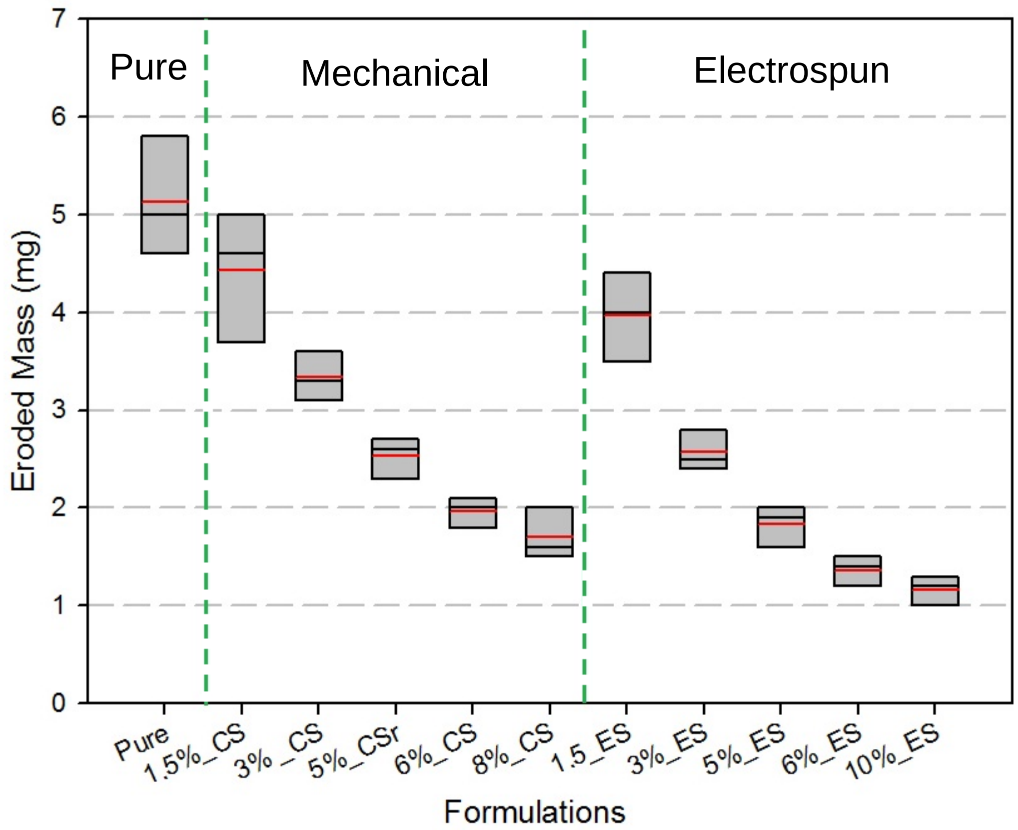
Mechanical



Electrospun

Effect of synthesis method

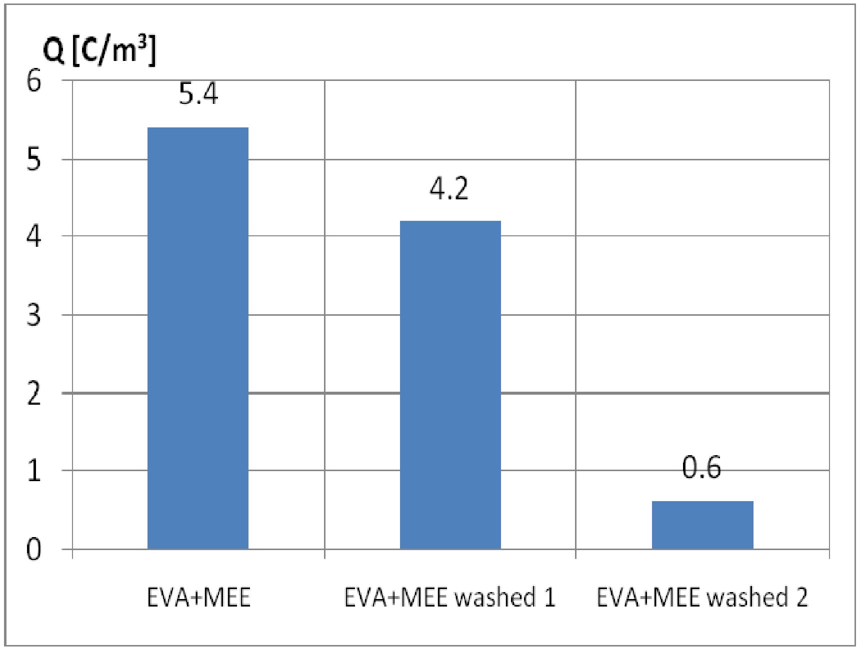
Comparison of surface erosion for SIR samples with silica filler, prepared with electrospinning compared to mechanical mixing



Effect of contaminants

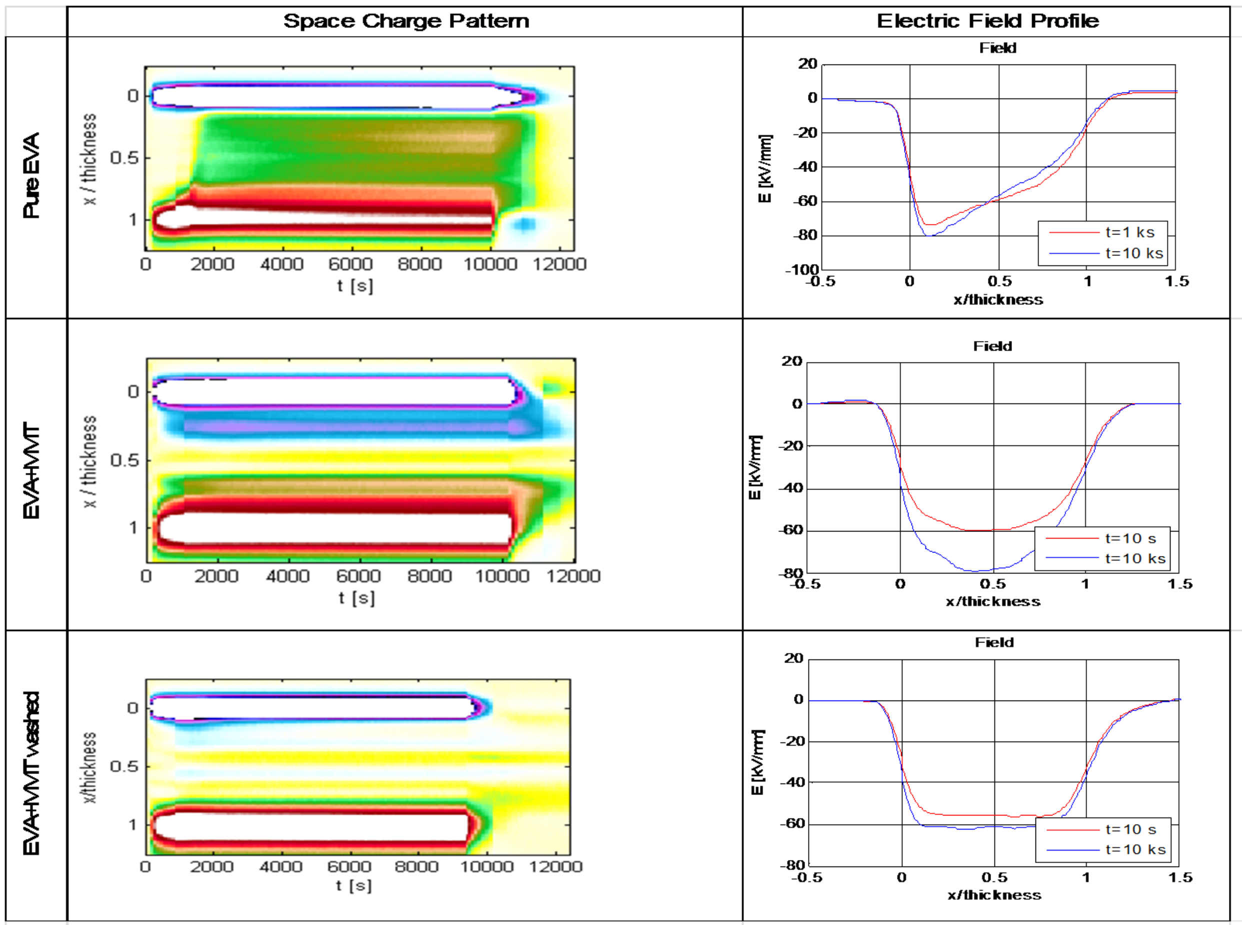
Ionic species

⌘ Present in the NC (e.g. Na cations in case of MMT) or added during the compatibilization process affect largely electrical properties, in particular under dc voltage → washing treatments are required!



Maximum accumulated charge density after 1h of polarization under 60 kV/mm, EVA+MMT is the NC obtained from unwashed filler, EVA+MMT washed 1 is the NC obtained from filler subjected to the first step of the purification treatment, EVA+MMT washed 2 is the NC obtained from filler subjected to both steps of the purification treatment

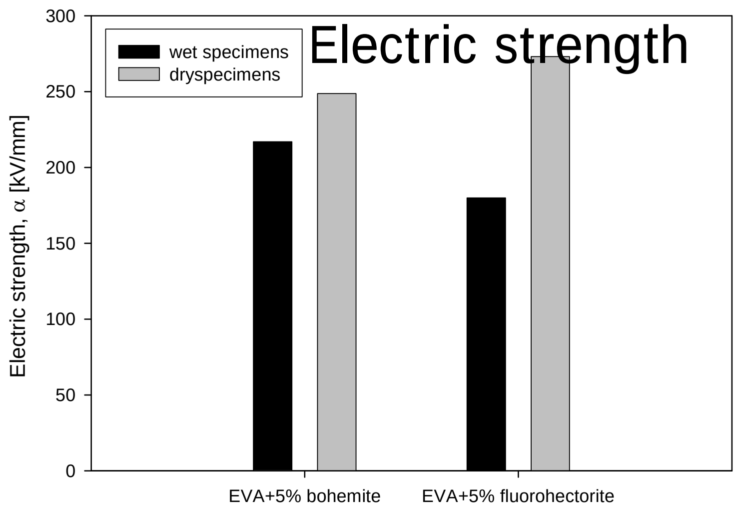
Effect of contaminants



Effect of moisture

Moisture

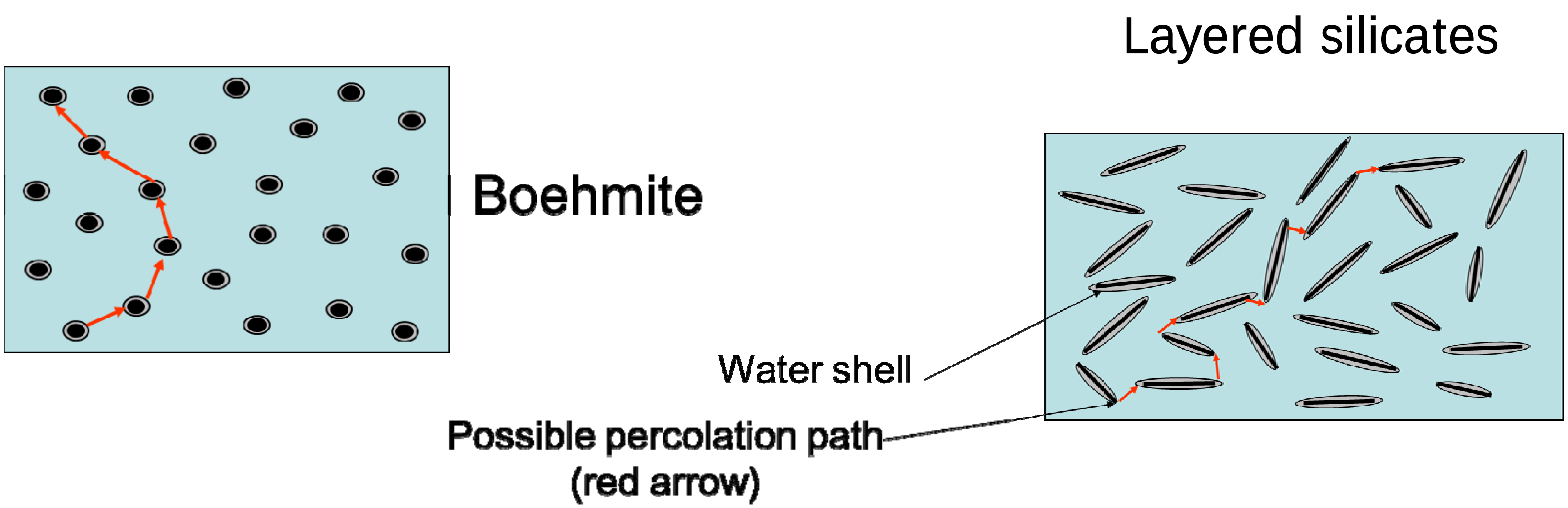
- Water adsorbed by the filler particles (if hydrophilic) before the manufacturing process surrounds the filler particle as a thin shell in the final NC.
- The exposure to a humid environment after the manufacturing process may cause the adsorption of water in the NC particularly if the polymer is hygroscopic (e.g. epoxies or EVA).
- This may have a significant impact on NC electrical properties



Any effect of the nanoparticle aspect ratio ?

Effect of moisture

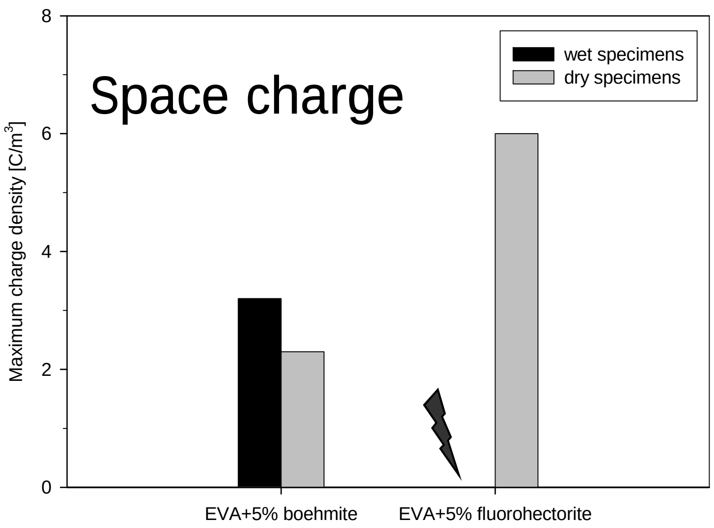
Moisture: effect of the aspect ratio



⌘ Percolation paths are more probable in NC having nanofillers with higher aspect ratio

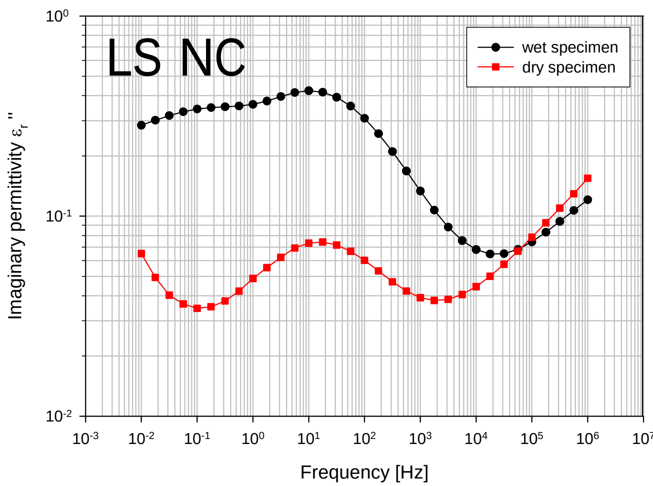
Effect of moisture

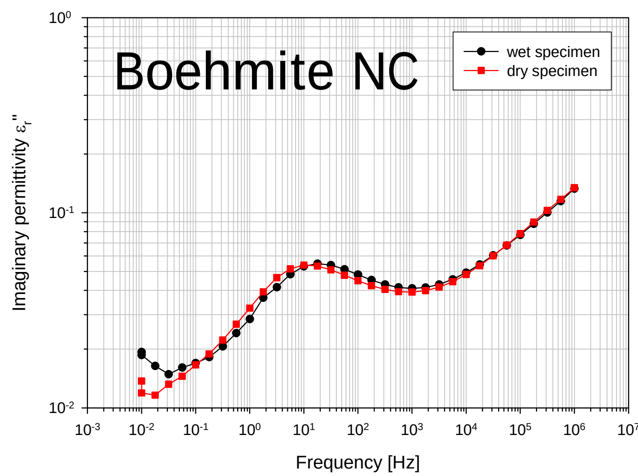
Moisture



Maximum stored charge density for wet and dry NC specimens. Nanofillers: boehmite (5%wt) and layered silicate (5%wt). Electric field =60 kV/mm. The arrow indicates that the test was not completed due to specimen breakdown.

Permittivity (imaginary part)





Summary

- Main problem is to achieve a good dispersion and distribution of nanoparticles in the host material; compatibilization with host material required
- Particle type, size and aspect ratio have impact on NC properties
- Different synthesis methods have an impact on the dielectric behavior
- Contaminants and moisture have a strong impact on dielectric properties of nanodielectrics