P2 THROUGH NANOTECHNOLOGY

SEPTEMBER 25-26, 2007

University of Strathclyde Glasgow

Environmentally Friendly, Nano-based Polyurethane Fire Retardant Systems

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"Pollution Prevention through Nanotechnology"
September 25-26, 2007, in Arlington , VA

WestCHEM

Challenge

- To create a flexible polyurethane foam from environmentally friendly fire retardants.
- Eliminate the current favourite fire retardants are based on halogenated phosphate esters form the formulations.
- Product should be a flexible foam which does not drip when burnt.

Are nano materials new and exotic?

- Historically one of the oldest materials know to man has been **clay,** this is a **nano material.**
- Clay is found all over the world and is very cheap. It has been used in a variety of applications for thousands of years.
- Why is clay considered a **new** nano material?

Dispersion of clay particles

Clay is produced naturally as a layered structure with sheets which are ~1 nm thick and extend in there other directions for distances of the order of between 100 to 1000 nm.

In its natural form clay is stacked into columns and has a pseudo spherical form i.e has a particles size of the order of 1- 10 microns.

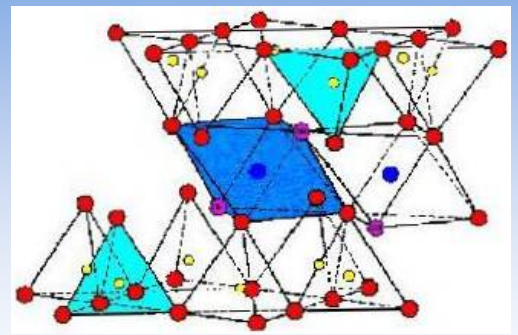
Particles of clay do not enhance materials properties very effectively.

Dispersion of the clay particles creates a nano material

A common feature of all problems concerned with nano materials is the ability to disperse the nano particles in a controlled manner through the material.

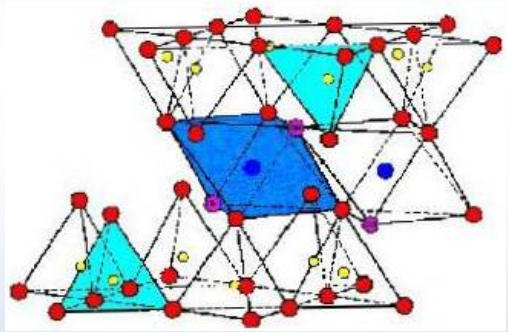
The property enhancement which can be achieved are associated with the correct dispersion of the nano material **- clay**.

Crystal structure of clay materials?



Na^+ Na^+ Na^+ Na^+

9Å



< tetrahedral

<octahedral

< tetrahedral

Aluminosilicate clays - $M^+_y(Al_{2-y}Mg_y)(Si_4)O_{10}(OH)_2nH_2O$

Montmorillonite Clays

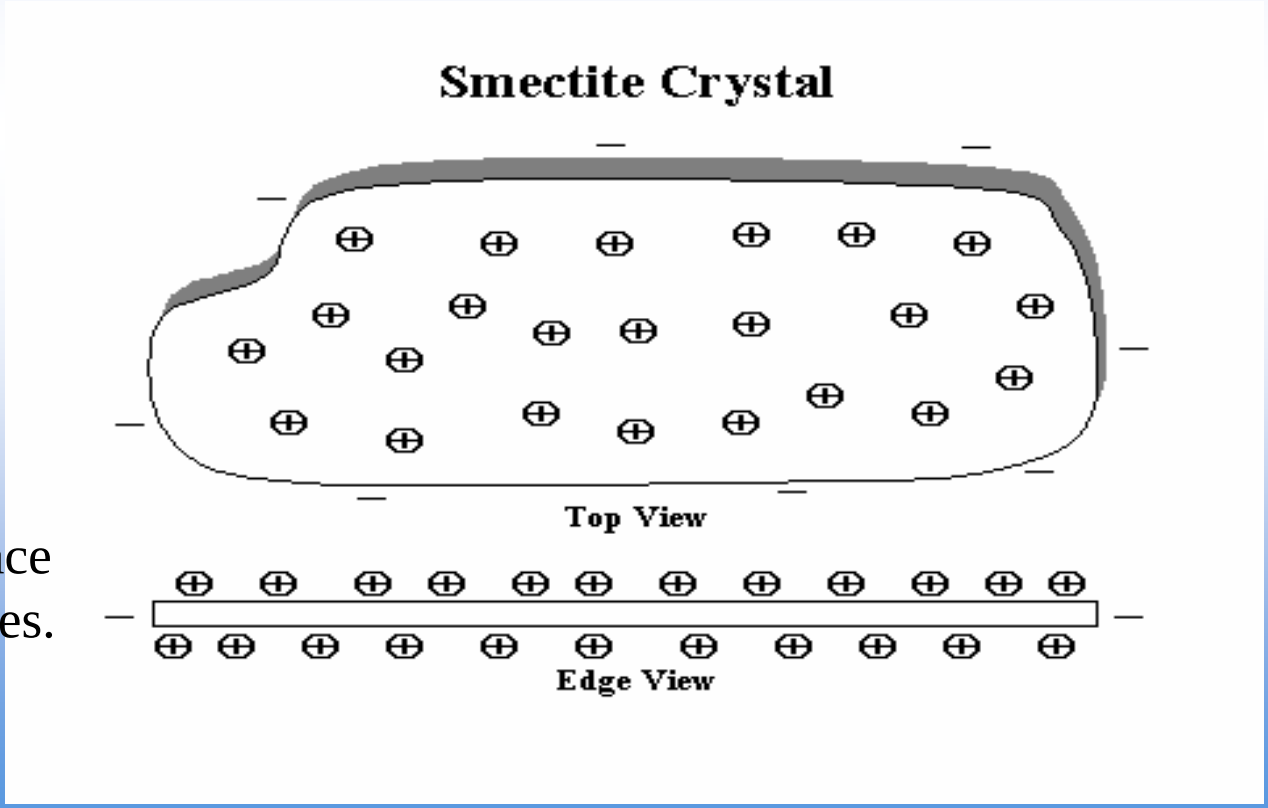
o - Al, Fe, Mg, Li [defect cations] **o - Na^+, Rb^+, Li^+,Cs^+ [Exchangable cations]**

Montmorillonite Clays

Stack of clay particles;

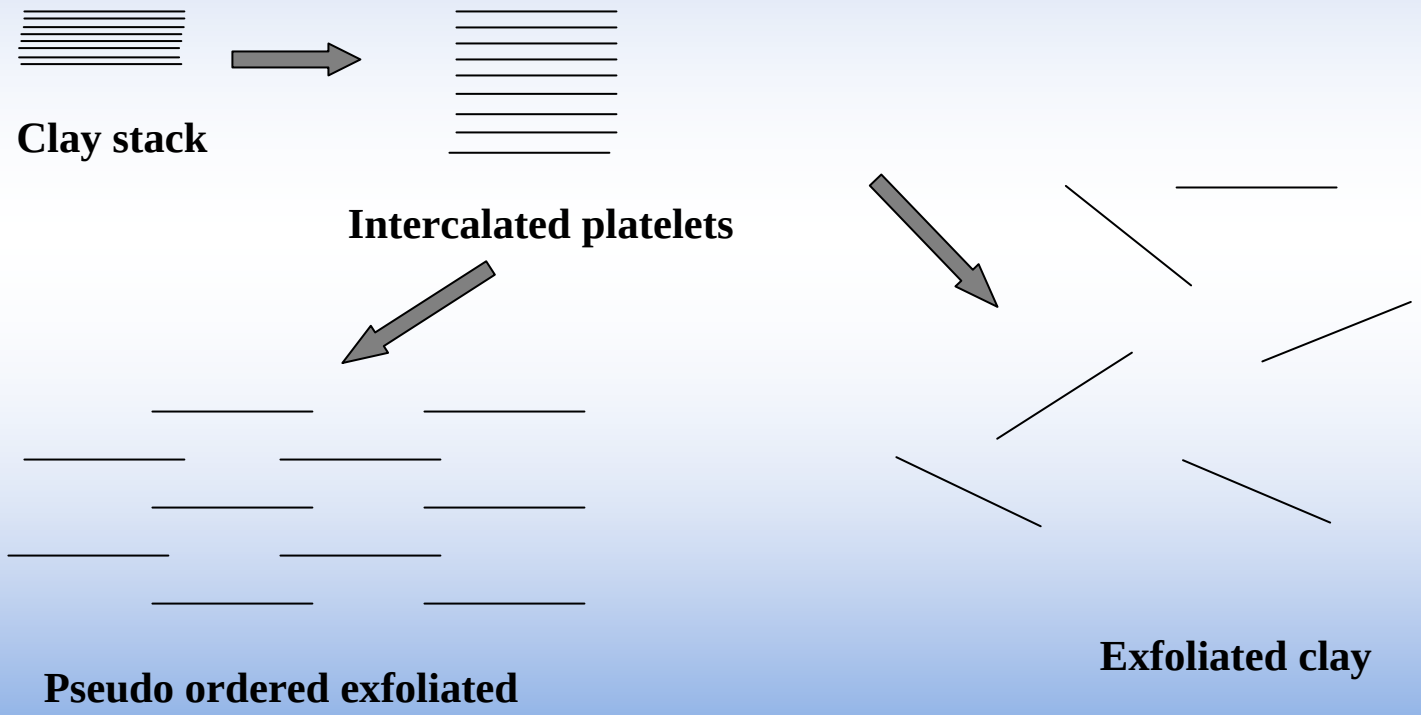
the columns will also organise

themselves into more spherical structures

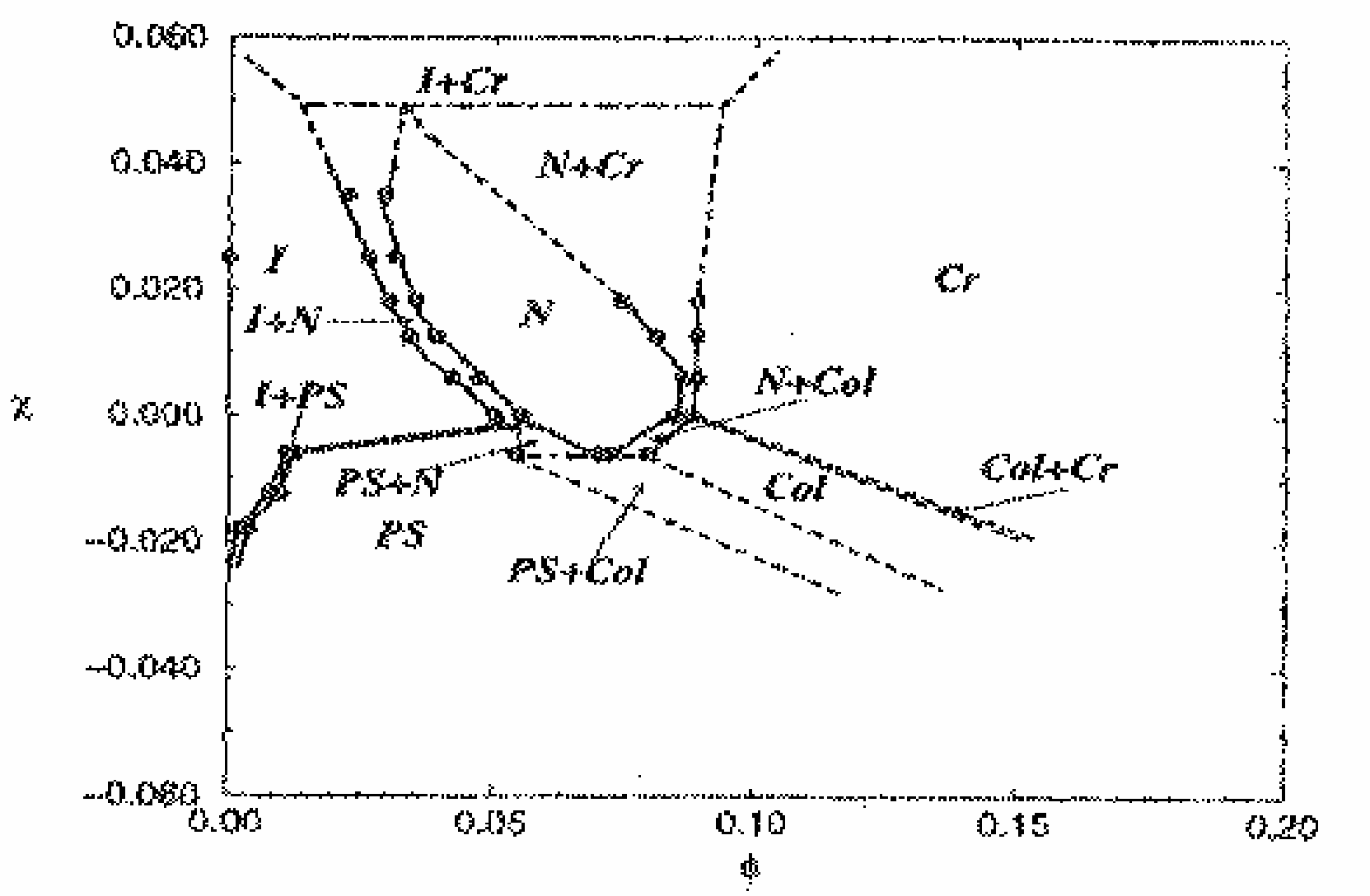


The charges shown in the diagram are the balancing counter ions. The sites are anionic in the surface and cationic on the edges.

Creation of Nano scale structures from Layered Silicate Nano Composites



Phase diagram for exfoliated clay



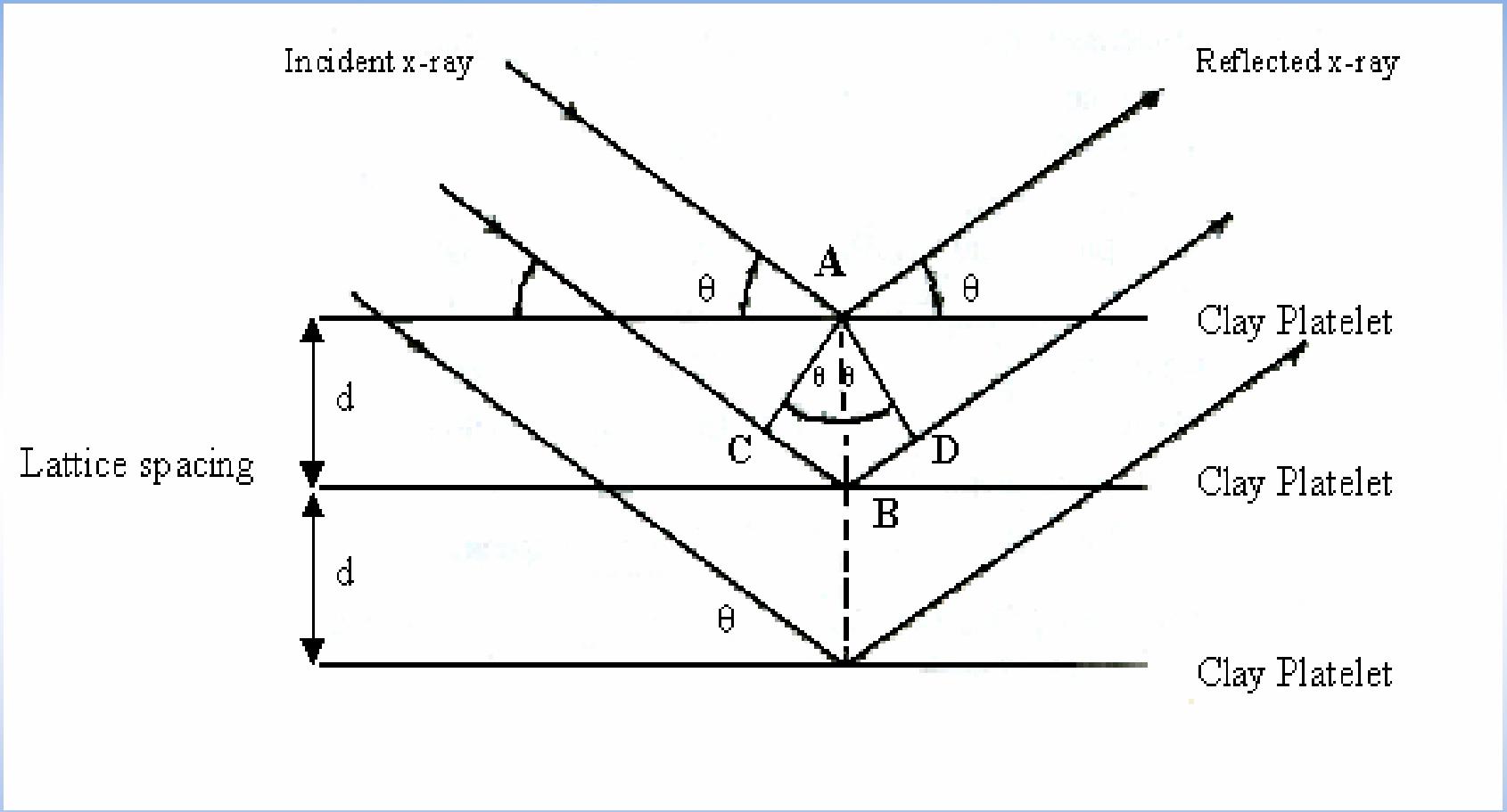
I – isotropic; N- nematic; PS – plastic solid;Cr – crystalline; Col –columnar

How can we study the structure at the nano level?

We have used two approaches:

- X-ray scattering form ordered structures.
- Rheology for characterising the liquid state.

Wide Angle X-Ray Scattering

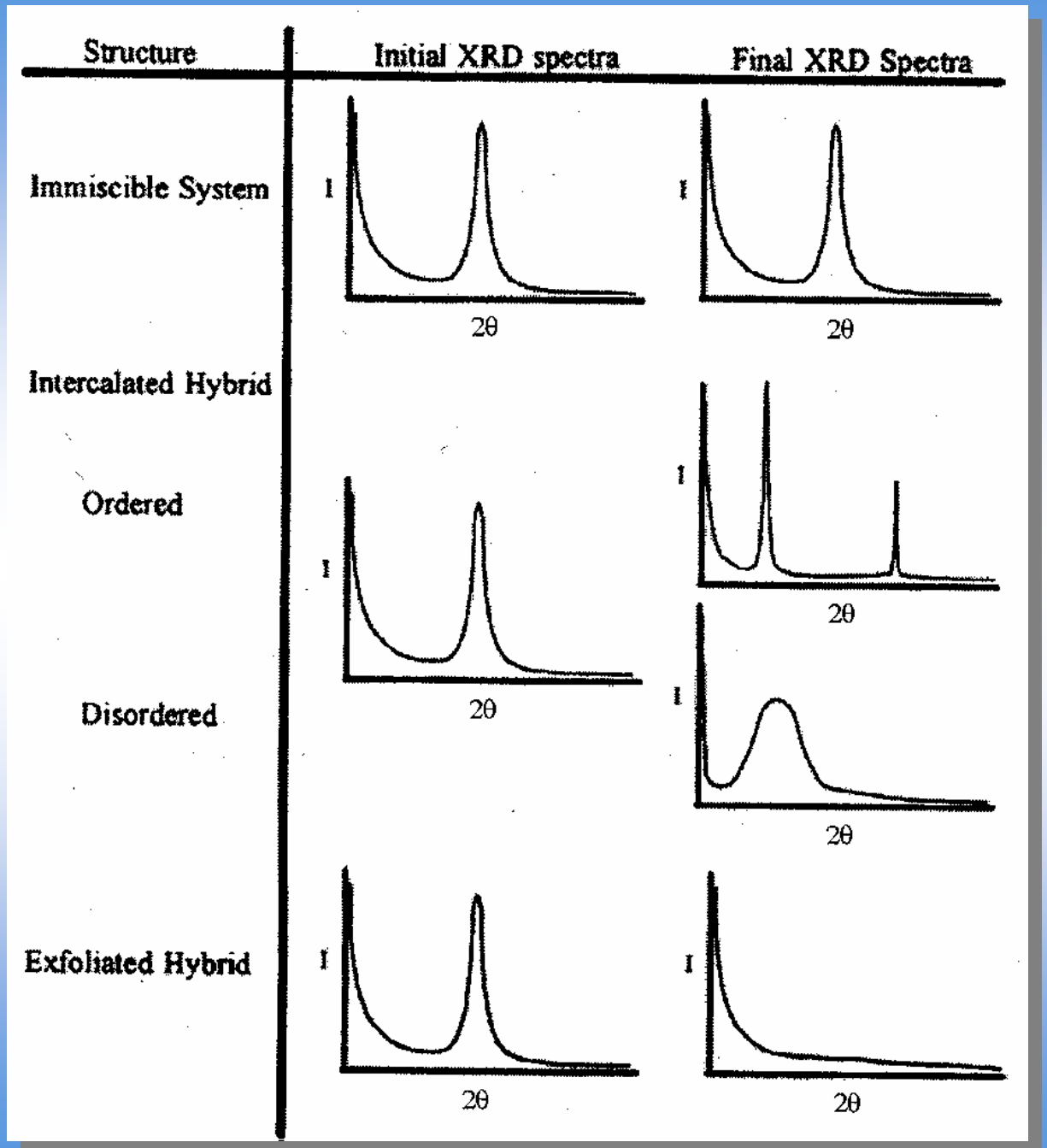


AB = CB/ sin θ

AB = CDB/ 2sin θ

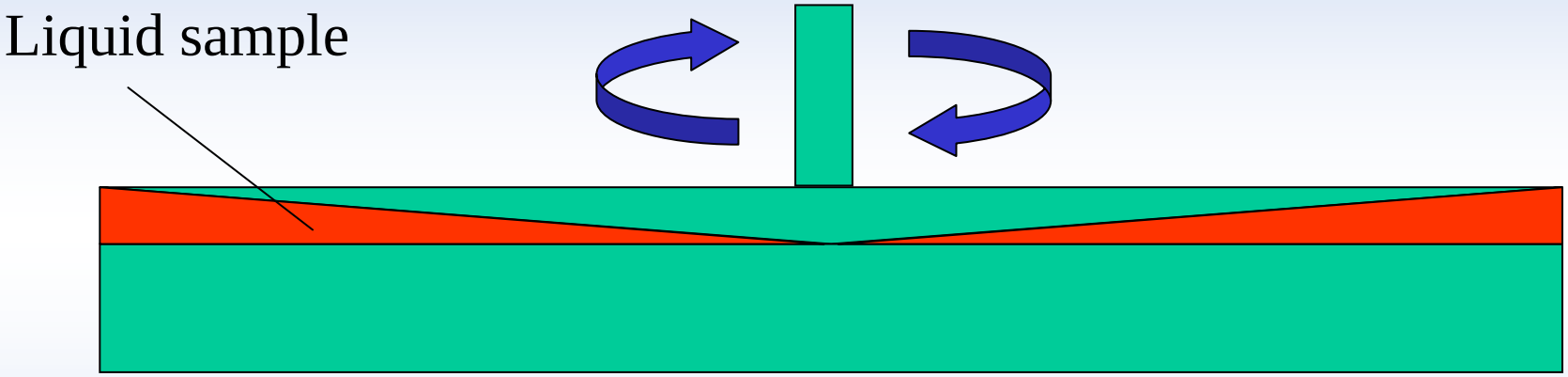
Schematic of the general X-ray scattering from a clay platelet

Schematic of powder X-ray diffraction spectra for nanocomposites



R.A.Vaia in 'Polymer - Clay Nanocomposites', T.J. Pinnavaia & G.W.Beall (eds), Wiley, 2000.

Rheological Measurements

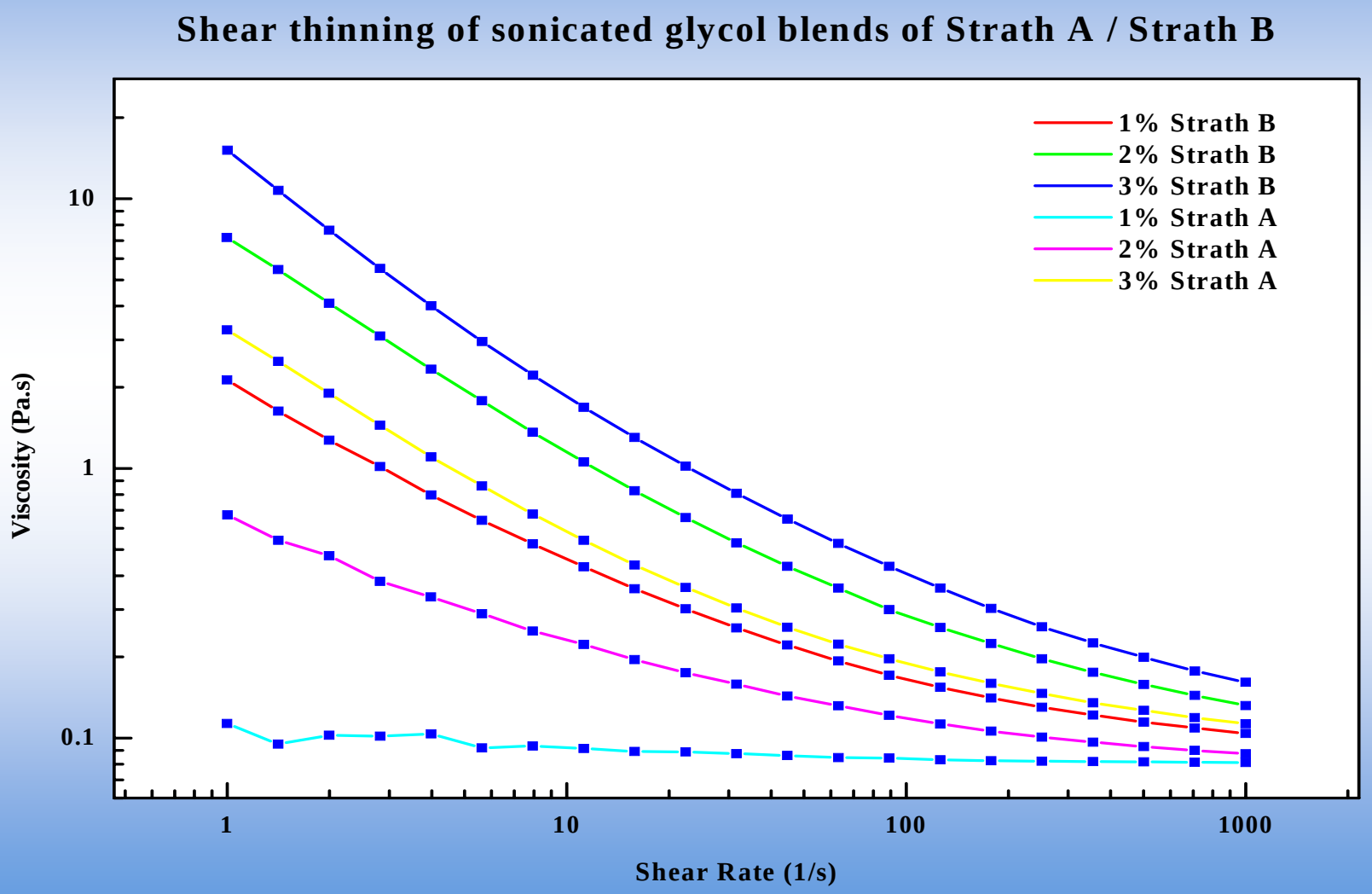


The plates are rotated at different speeds and allow the viscosity to be calculated at different shear rates.

What is the best method of dispersion of the clay particles?

- Low shear mixing does not always provide sufficient energy to produce an exfoliated state in the liquid phase.
- High shear mixing can sometimes achieve partial exfoliation of the clay particles.
- Ultrasonification of the dispersion usually will achieve exfoliation of the particles.

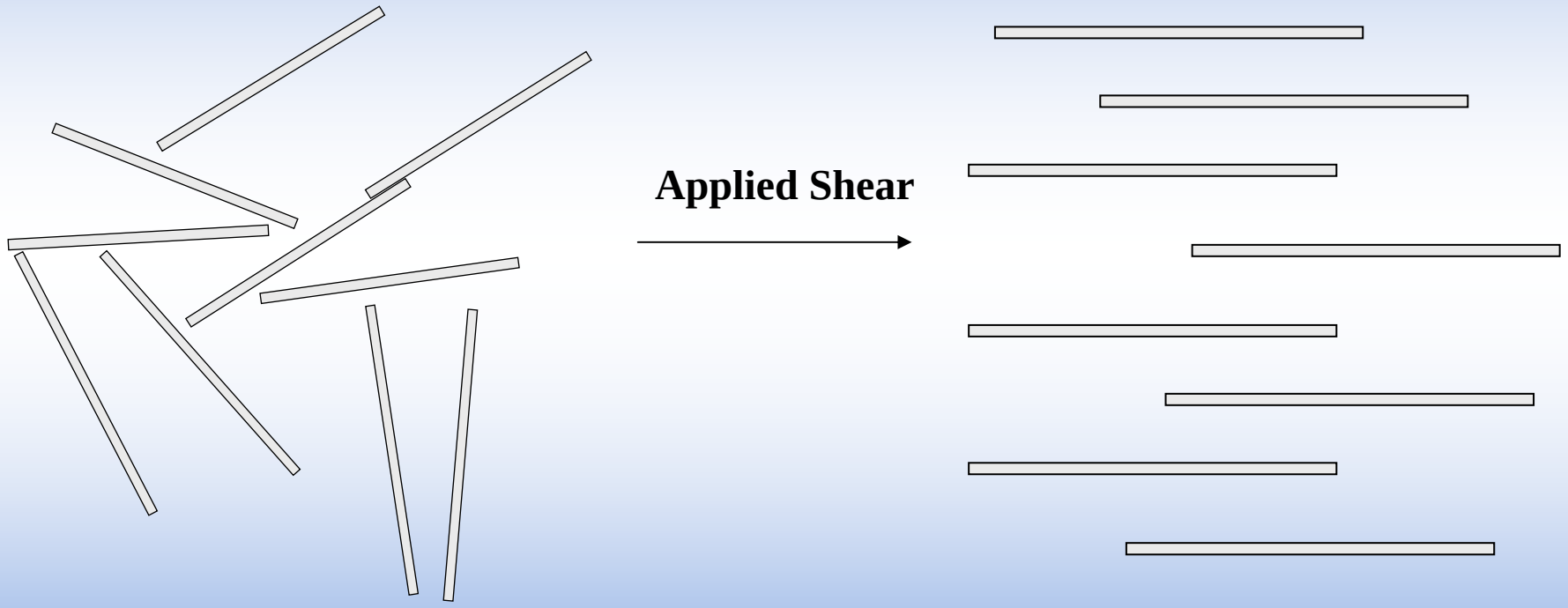
Effect of dispersion methods -study of PU monomers



Why do we see are large increase in viscosity?

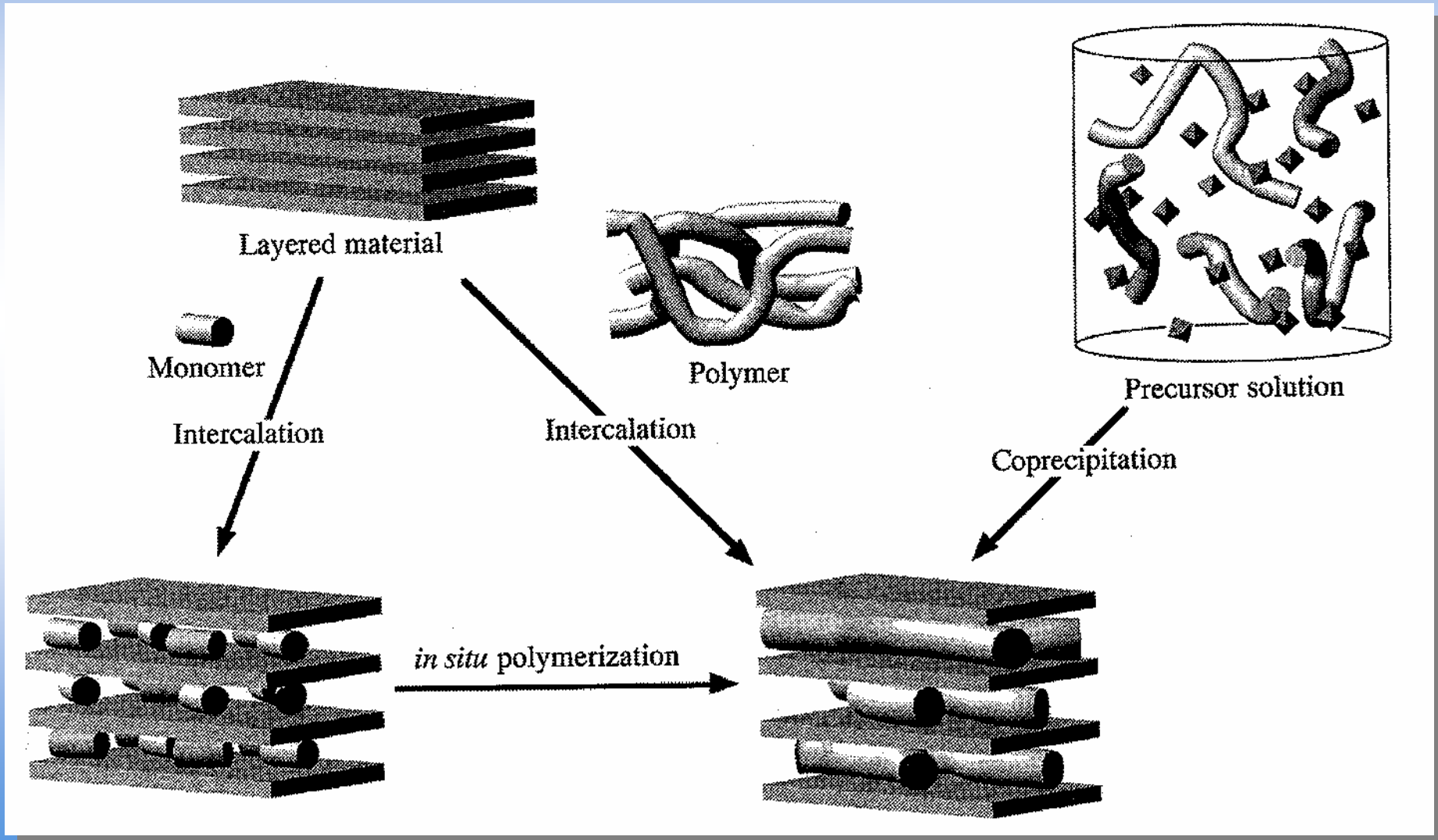
- Clay particles dispersed in a liquid will not produce a very viscous mixture.
- The viscosity arises from the exfoliated plates forming a ‘log jam’ type of structure in the liquid.
- As the shear rate increases so the platelets interactions cease to be able to contribute to the viscosity and it falls to that of the basic fluid.

Alignment of Platelets Due to Shear



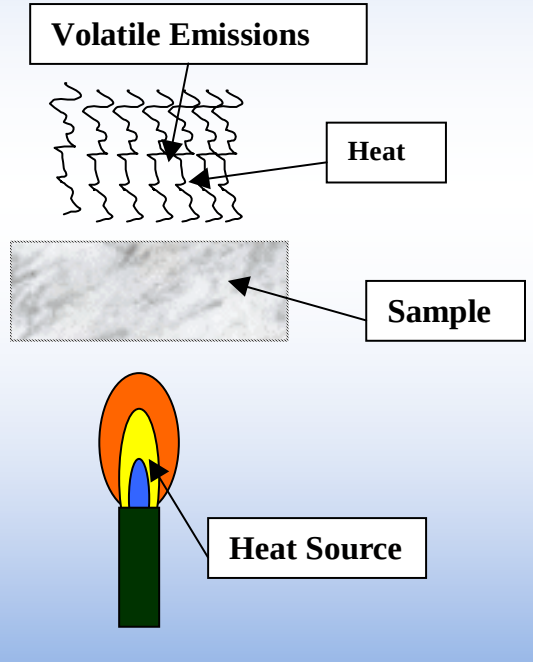
Alignment of the platelets in the shear field leads to a lowering of the viscosity.

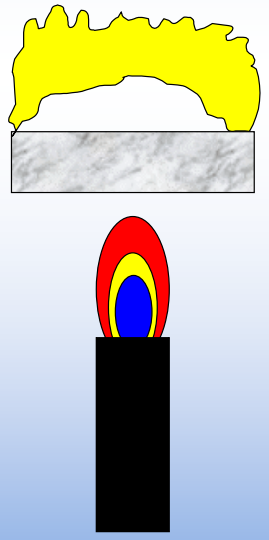
How do we use exfoliated clay to create new materials?

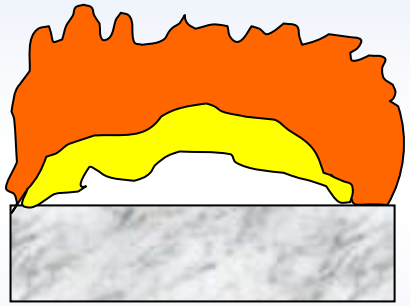


Fire - How does it start and propagate?

Heat can melt the sample and cause ‘dripping’ of flaming molten material which can cause a fire. Loss of rigidity is a cause for fire spreading in electrical insulation fires.







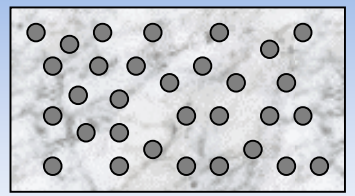
Precombustion - - Initiation of combustion - - Self sustained combustion

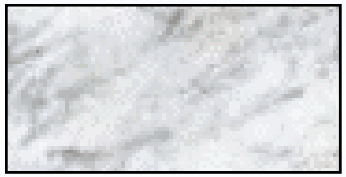
- rate of volatile emission.
- volatiles exceed spontaneous ignition temperature.
- radiant heat enhances degradation and volatile emission
- molten polymer allows transfer of heat to un-degraded material.

Fire - How to stop fire propagating?

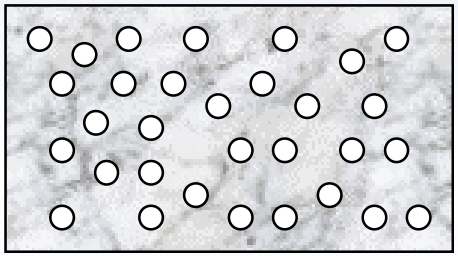
Illustrations of various inhibition mechanisms.

Heat sink -aluminium hydroxide →





Intumescent →



Nanocomposite + char formation.

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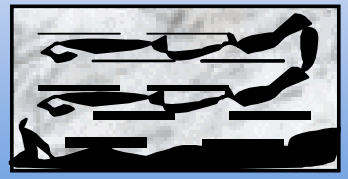
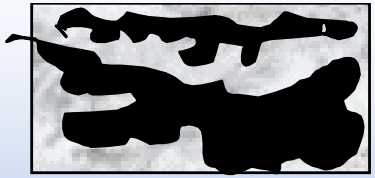
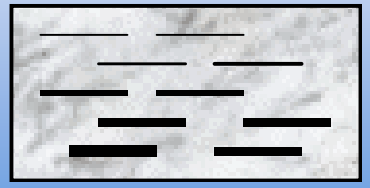


Char formation →



Nano composite →



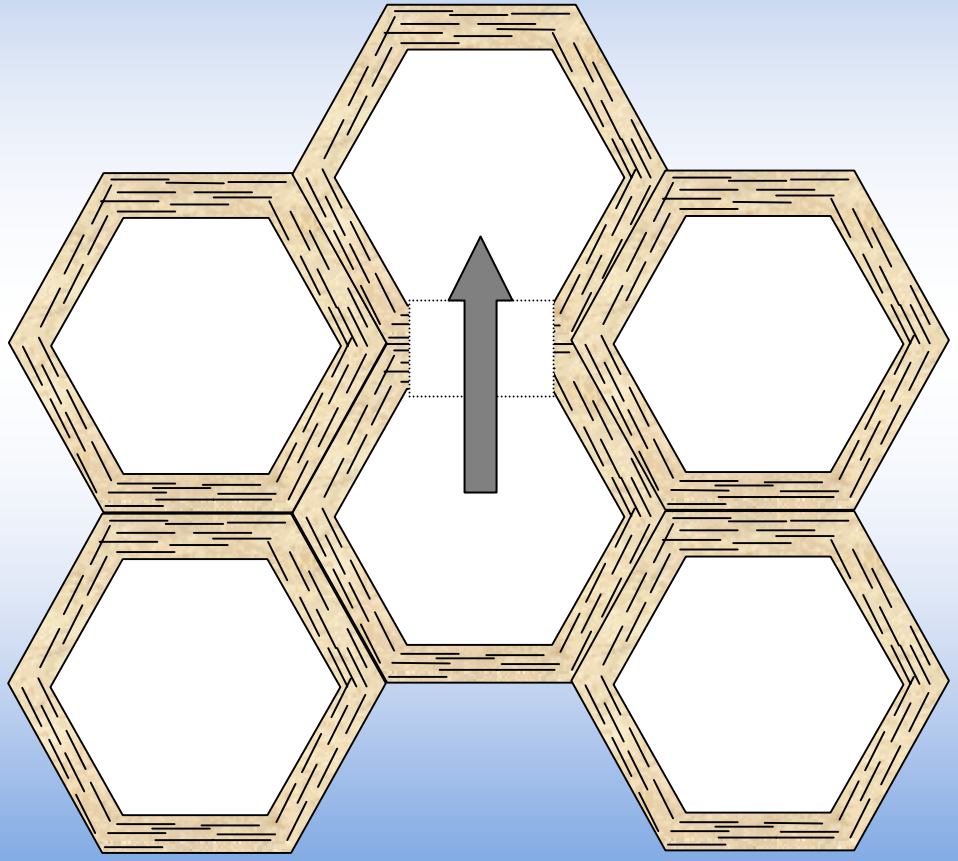
What are the desirable qualities of flexible polyurethane foams?

The foam should be:-

- flexible and compliant to a load being applied. The level of the compressibility of the foam is critical to a good feel factor.
- The foam should rapidly recover once the load has been removed. The foam should demonstrate a high degree of resilience.
- The foam should show a low flammability when exposed to a naked flame or heat source.

Flame Retardancy in Polymer Foams.

Nano platlets composite structures within cell walls to inhibit volatile diffusion and enhance the viscoelasticity of the melt phase .



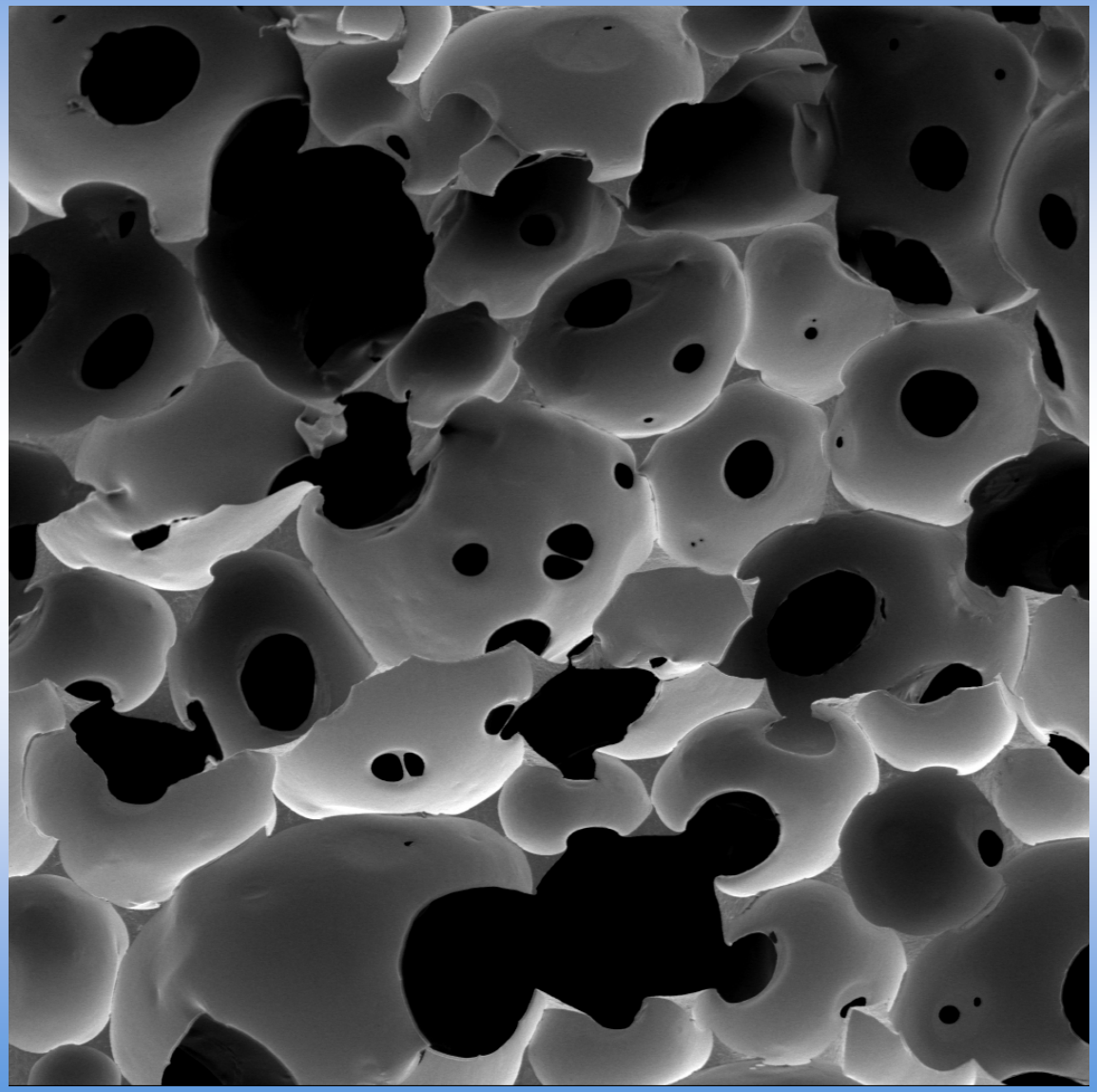
Flexible Foam Systems

- A series of flexible foam system have been produced with the required flexibility and incorporating nanocomposite organically modified clay materials. {Patents have been applied for these systems}

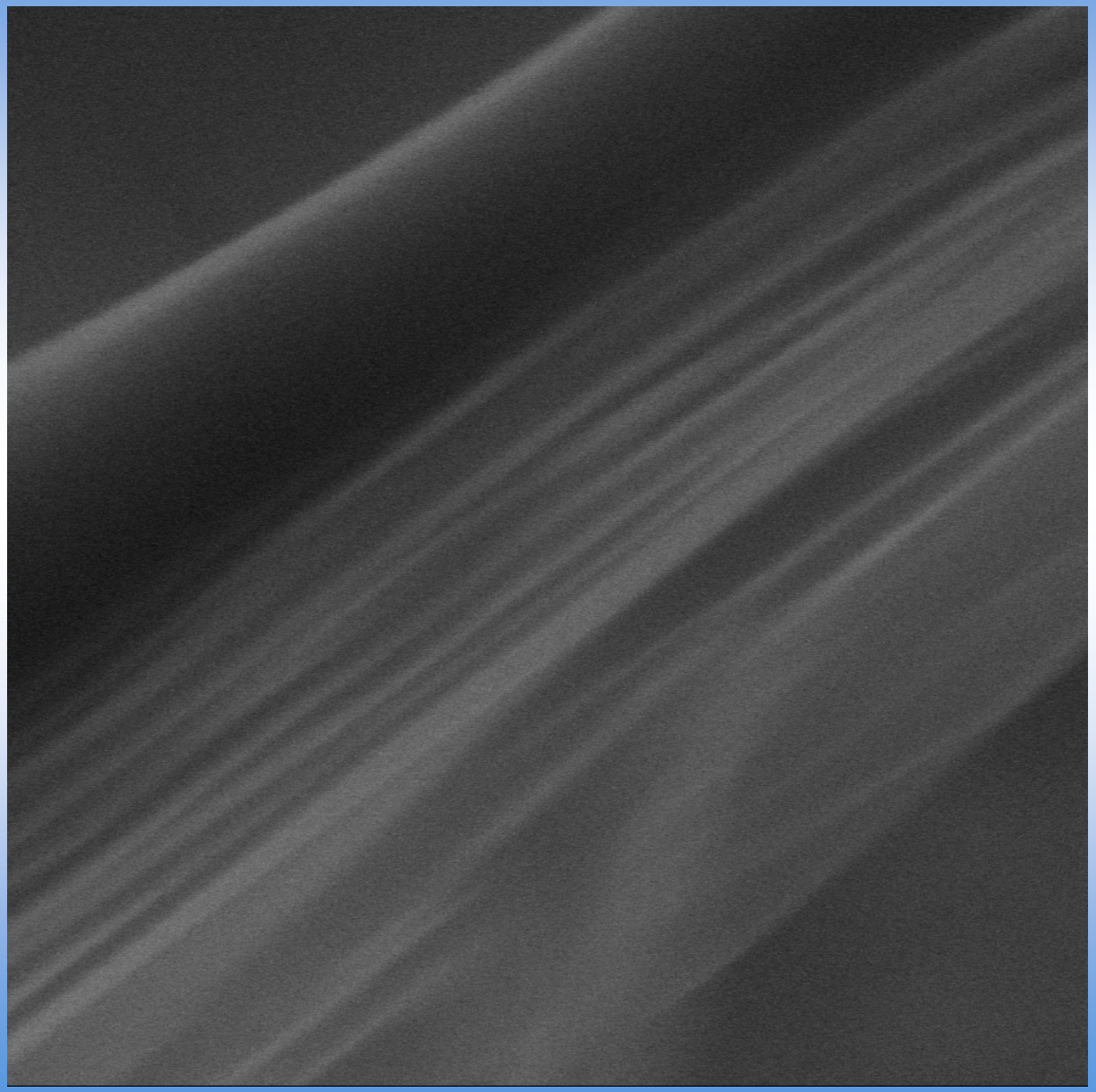
What do the materials look like?

- Electron microscopy has been performed and they show the nano material is present in the foam walls and has effected the rheology in the foam formation
- The materials have comparable mechanical properties to current flexible foam formulations

Electron Micrograph of PU foam



Electron Micrography of PU Foam Structure



Crib 5 Testing

The Challenge:

To avoid this

Obtain this

Escalating | Self-extinguishing

From these

The Process:

Formulation design

Daly, Lewicki, Liggat, McCulloch, MacRitchie, Pethrick, Rhoney

Nano Composites

I hope this short presentation has shown that by recognising the natural nano dimensions which exist in **natural** materials it is possible to enhance the properties of conventional materials which we produce and achieve a greater use of these materials.

Nano composites are not all about new exotic materials but can be about using traditional materials more effectively.

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Thank you for listening

Any Questions?