# ‘Nano-Materials for Composites’

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# What do we mean by nano materials ?

Chemistry deals with molecules which have dimensions which are of the order of 0.1 to 10’s nano metres.

Polymers have dimensions which are typically 10’s to 100’s nano metres.

Combining materials which have one or more dimensions in the nano range creates a **nano materials.**

# Do nano materials have any engineering significance?

The nano materials bridge the range of molecular and micro scales and allows **connectivity** of interactions which enhance the mechanical characteristics of the composite.

**Molecular interactions** will range from 0.1 to 2nm, typical **fibre** reinforcement will involve dimension which are 0.1μm to mm.

**Nano materials** bridge 1nm to 1 μm scale and aid **stress** redistribution and transfer.

# Classes of nano materials.

We can identify a range of different nano materials:-

- **Clay** is found all over the world and is very cheap when exfoliated and **organically** modified becomes a nano material.
- **Glass platelets** can be created with dimensions in this nano range and have reinforcing characteristics which parallel those of clay.
- **Graphite** can be produced in a nano exfoliated form.
- Hollow **carbon nano tubes** with diameters in the nano scale but with lengths in the micron – millimetre scale can be created but are expensive.
- **Nano silica** can be created dispersed in reactive resins – epoxy with dimensions in the range 30-60 nm
- Certain **block copolymers** can phase separate and form **molecular nano composites**.

# Scope of talk

- Clay nano composites.
- Molecular nano composites.
- Other materials can be covered in discussion.

# Clay nanocomposites

Because clay is **widely available** and relatively cheap these materials are potentially **attractive for commercial** use in composite applications.

One Scottish company has had nano materials in its composite production for almost a year!

# 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.

Property enhancement is associated with the correct dispersion of the nano material - **clay**.

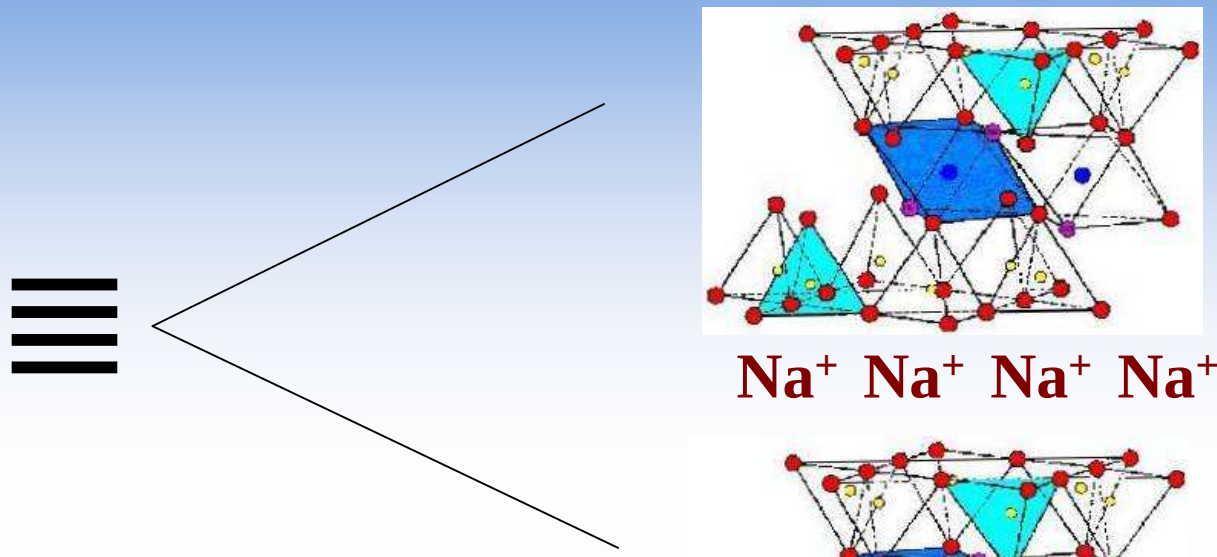
# Dispersion of clay particles

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

Clay naturally stacks in the form of columns and adopts a **pseudo spherical form** i.e has a particles size of the order of 1- 10 microns and **does not** enhance materials properties.

Exfoliated clay however does enhance physical properties.

# Crystal structure of clay materials?



$Na^+$ $Na^+$ $Na^+$ $Na^+$

9Å

< tetrahedral

<octahedral

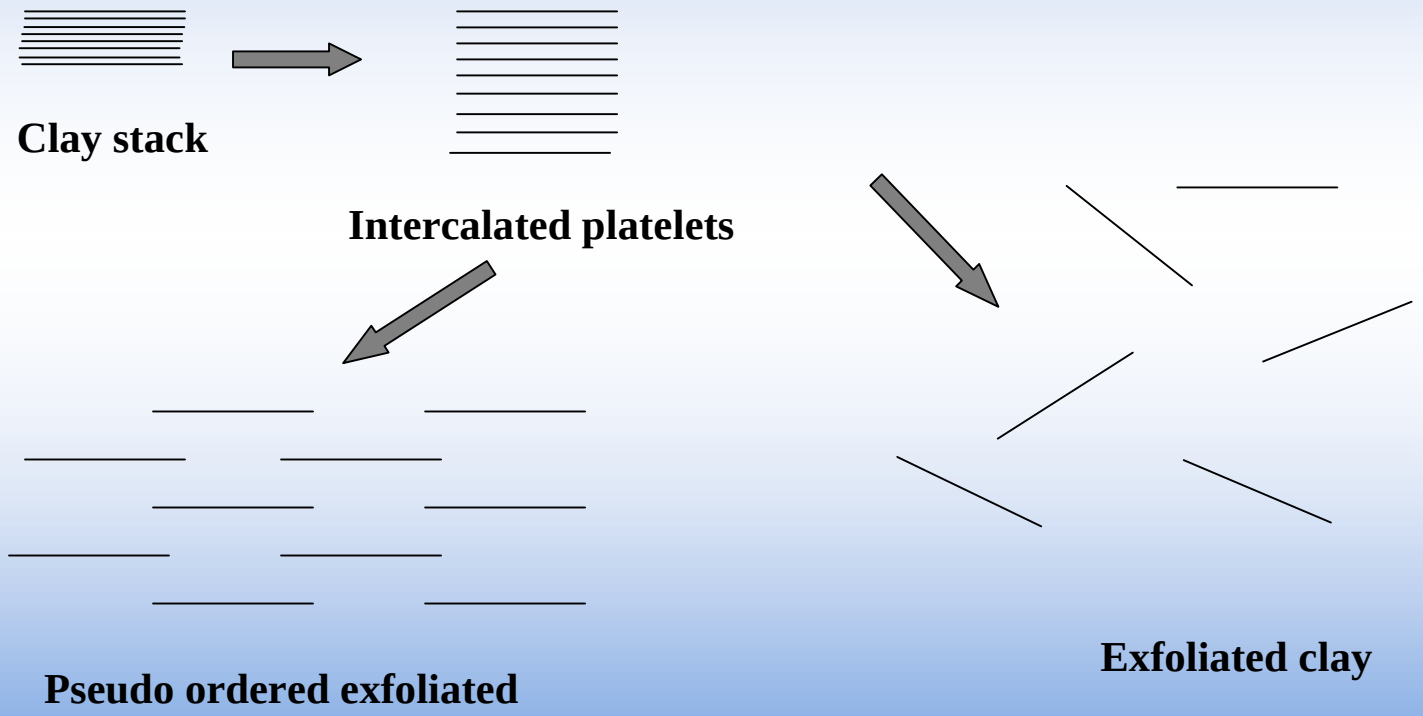
< tetrahedral

**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 ]**

# Creation of Nano scale structures from Layered Silicate Nanocomposites

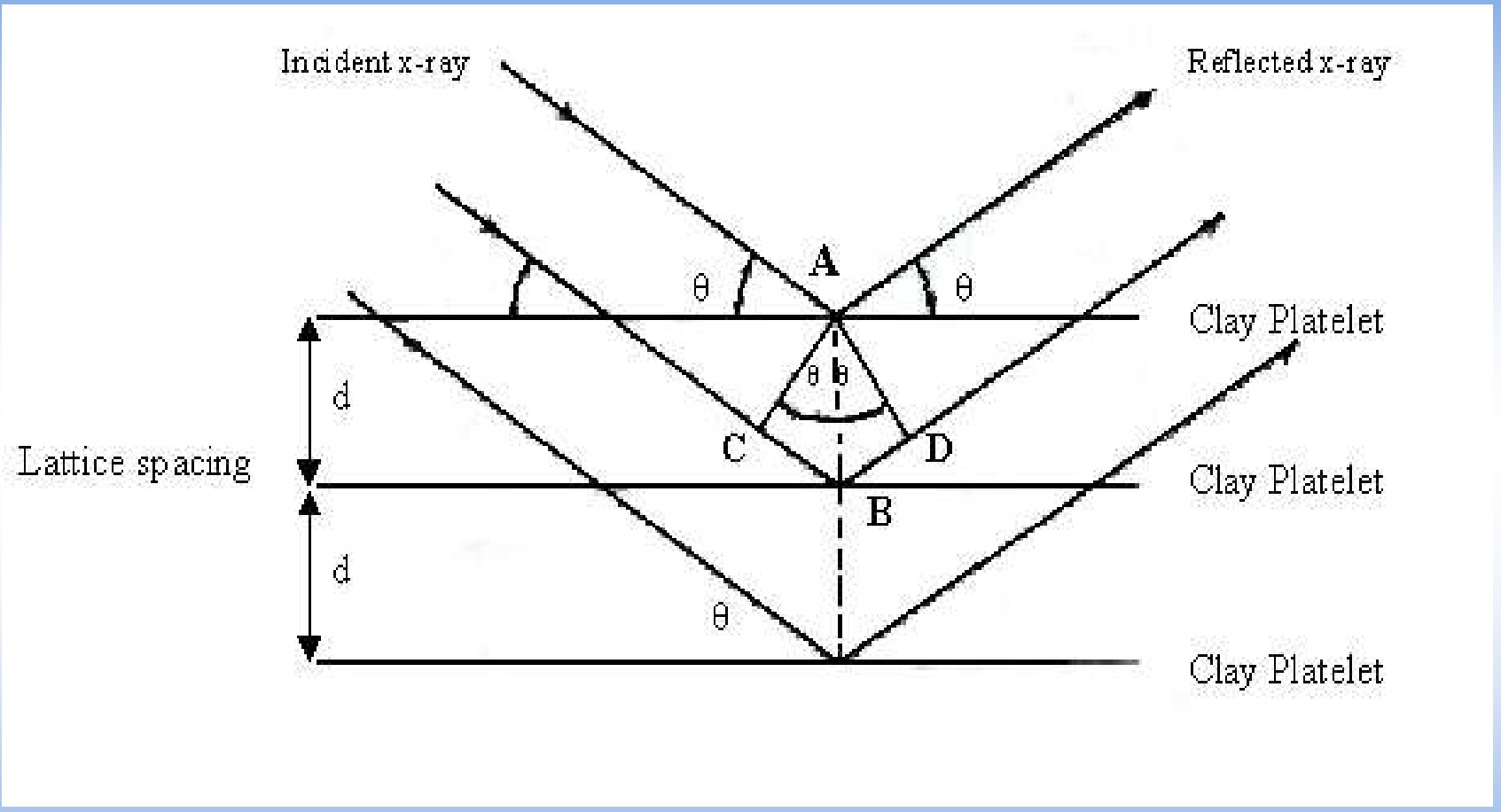


# How can we study the structure at the nano level?

We have used two approaches:

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

# Wide Angle X-Ray Scattering

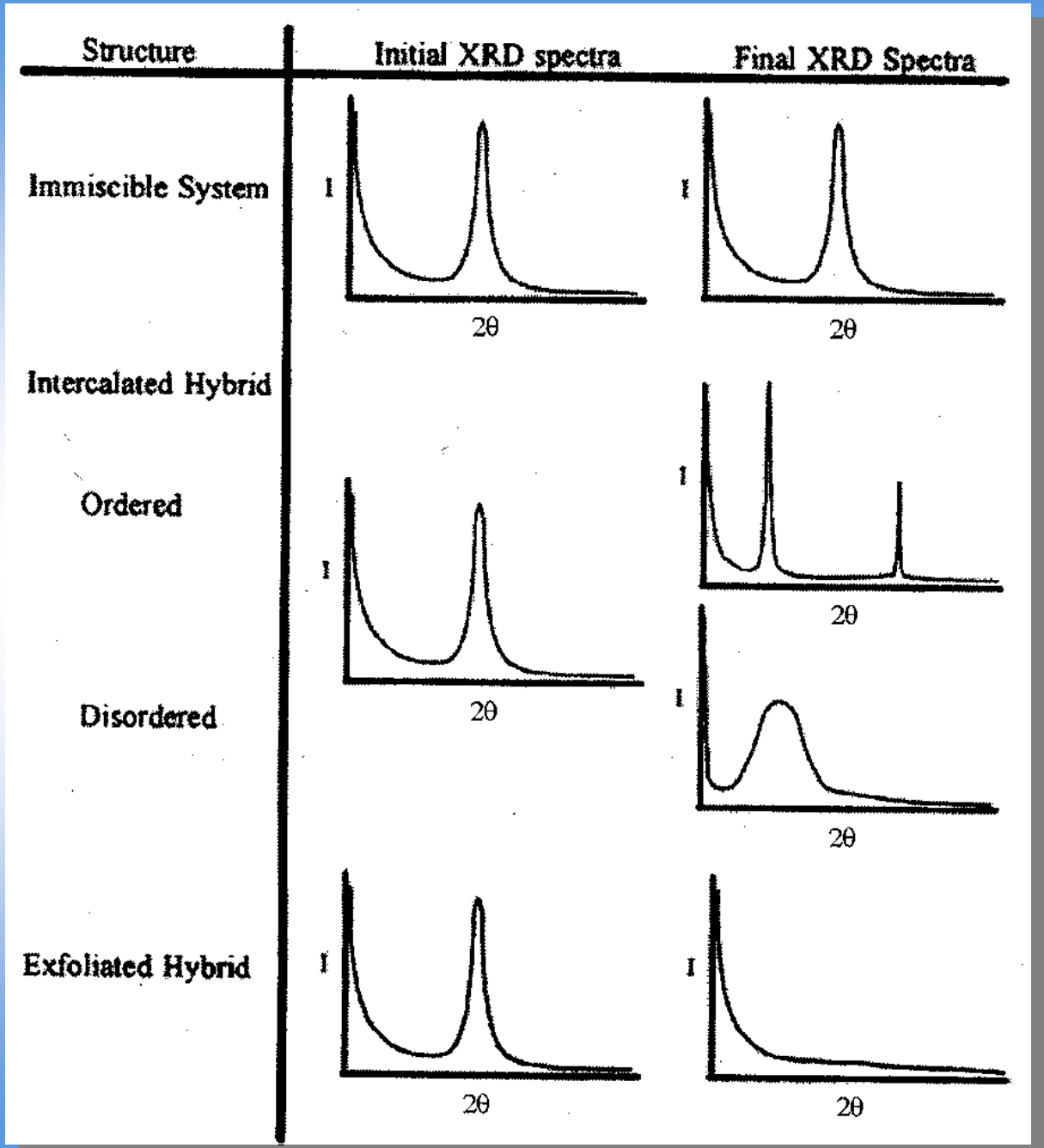



AB = CB/ sin θ

AB = CDB/ 2sin θ

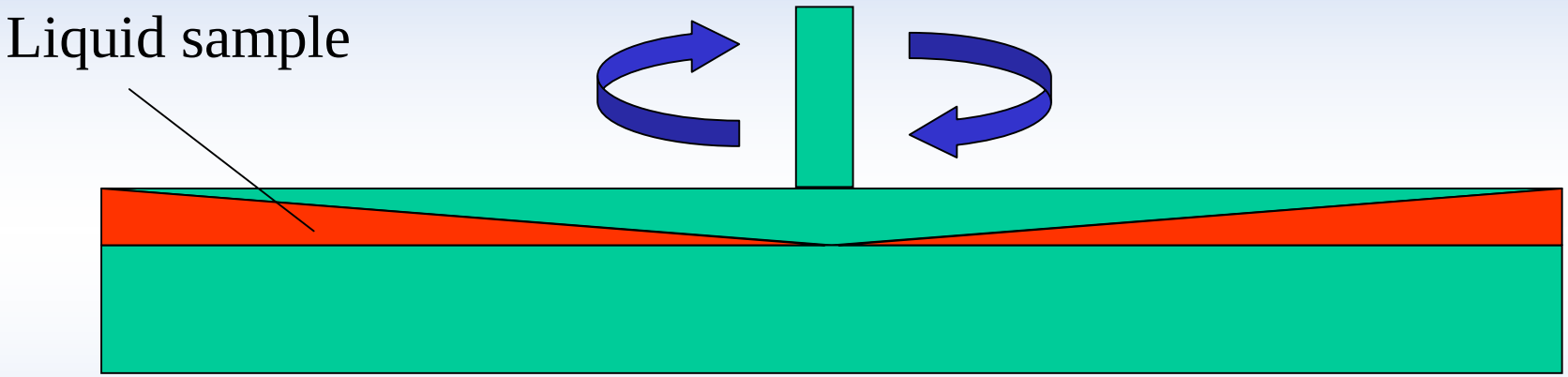
Schematic of the general X-ray scattering from a clay platelet

# 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

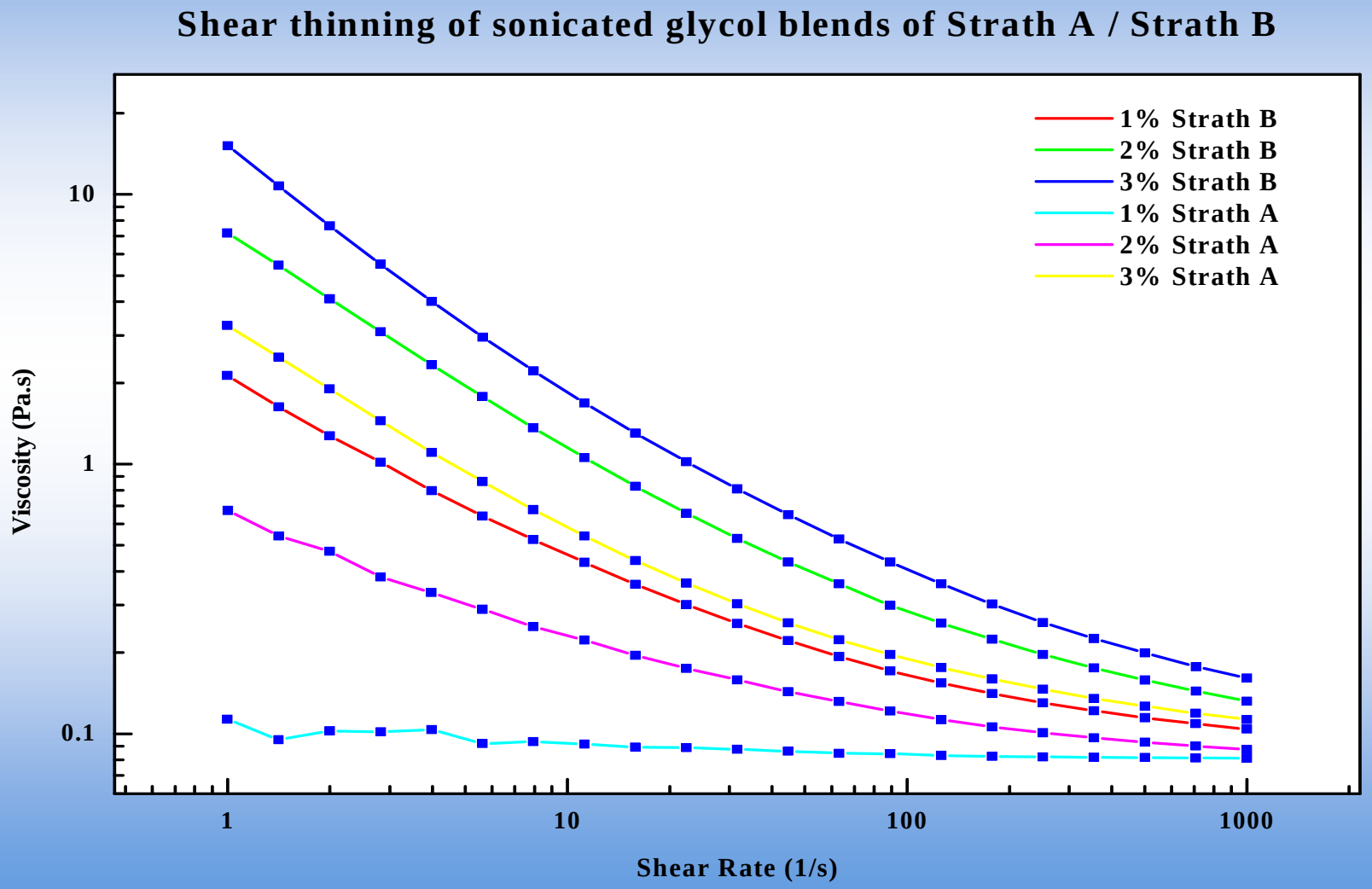



The plates are rotated at different speeds and allow the viscosity to be calculated at different shear rates.

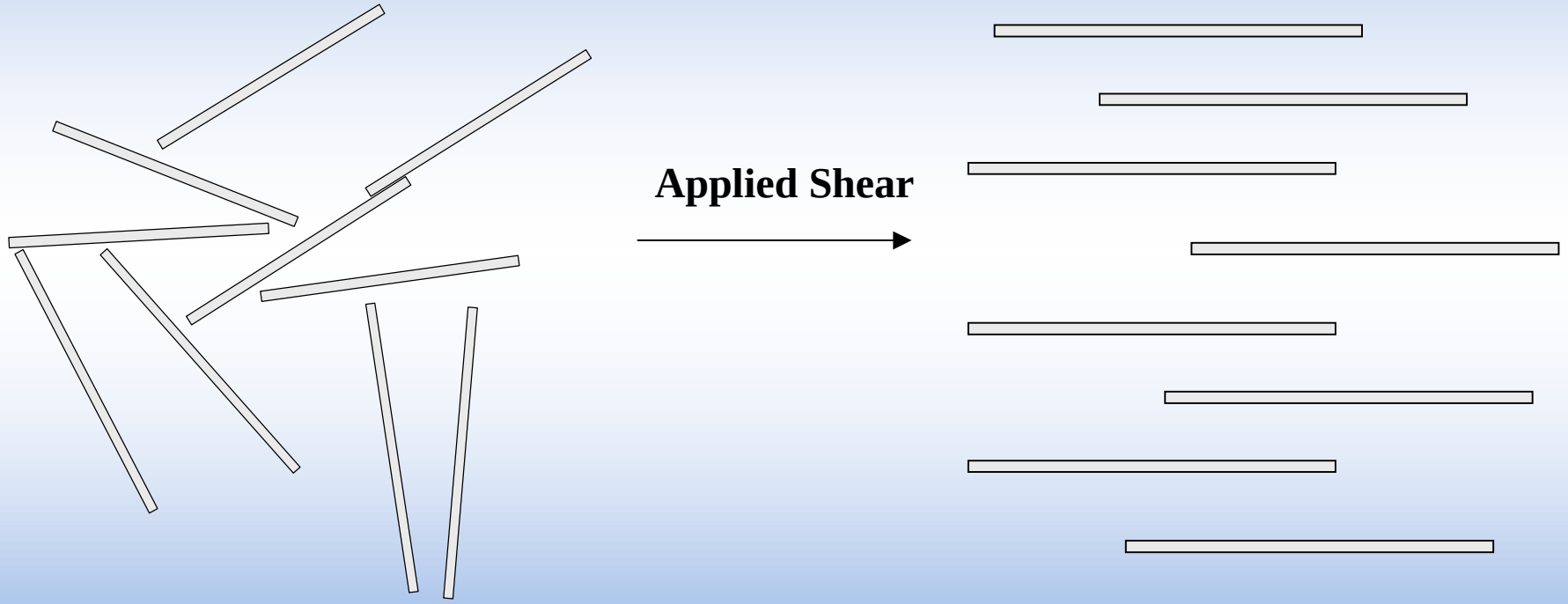
# What is the best method of dispersion of the clay particles?

- **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

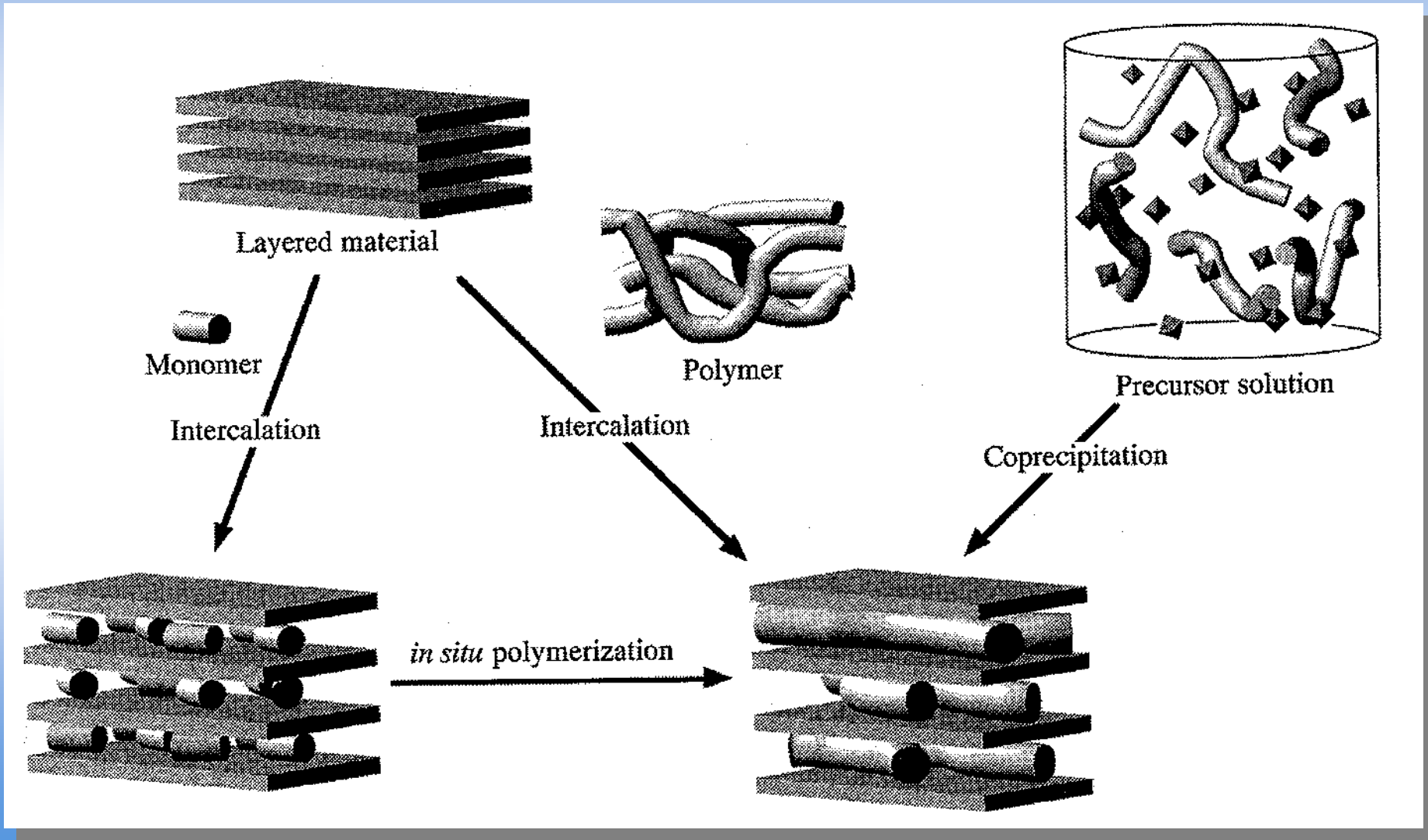


# Alignment of Platelets Due to Shear




**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?



# Target Materials

Two target materials:-

- An enhancement of the properties of an epoxy resin used in structural applications.
- A fire retarded foam material which is environmentally friendly

# Target 1 Epoxy Resins

Enhanced performance of epoxy systems through incorporation of nanoclay

# Epoxy resins

- Versatile properties
  - Highly flexible or hard and brittle
  - Retain strength over a temperature range.
  - Excellent adhesive
  - Electrical insulator

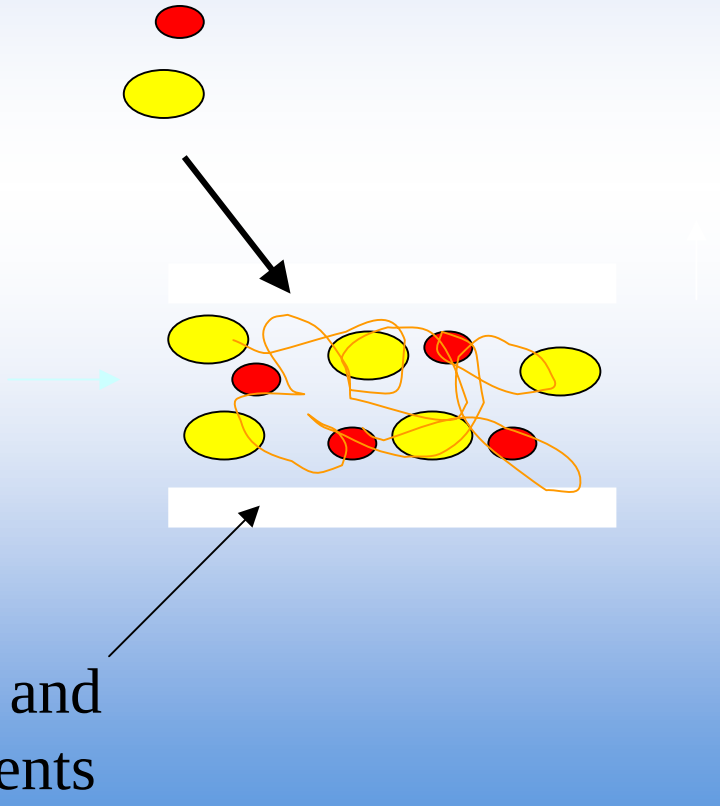
- Applications
  - Adhesives for aircraft
  - Surface coatings – decorative and/or protective
  - Electrical industry – protect from mechanical shocks through range of temperatures.

# Clay nanocomposites

- Addition of few weight % clay can lead to marked property improvements
  - Flame retardancy
  - Improved Tg
  - Increased strength
  - Decreased water/solvent uptake
- Reduction in polymer chain mobility
- Creation of tortuous pathway for moisture diffusion

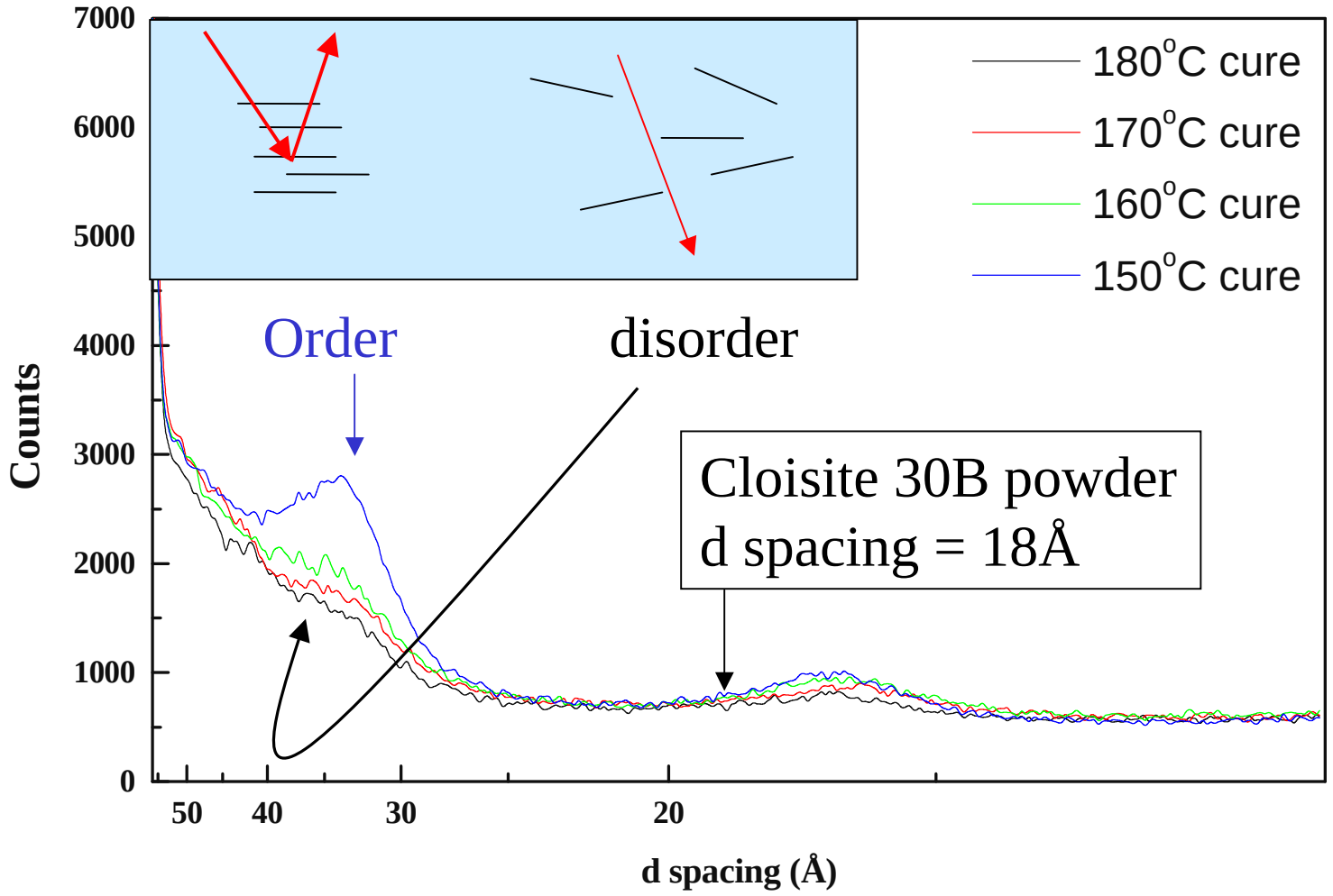
# Factors affecting dispersion

- The following effect the nature of the dispersion produced.
  - **Cure temperature**
  - **Cure agent**
  - **Degree of cure**
  - **Choice of epoxy resin**

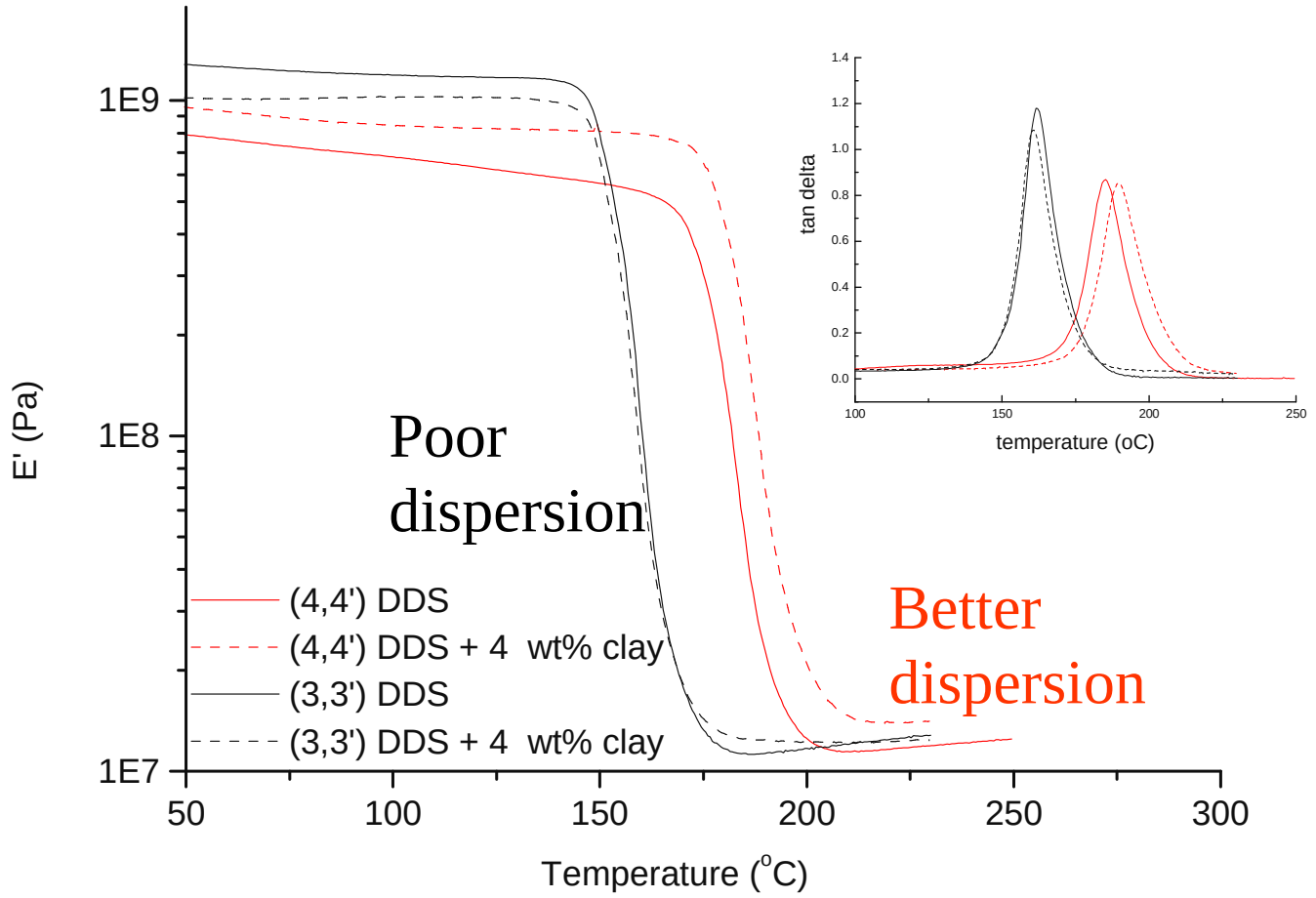


# XRD – Epoxy + 4wt% clay

## Cure temperature effects

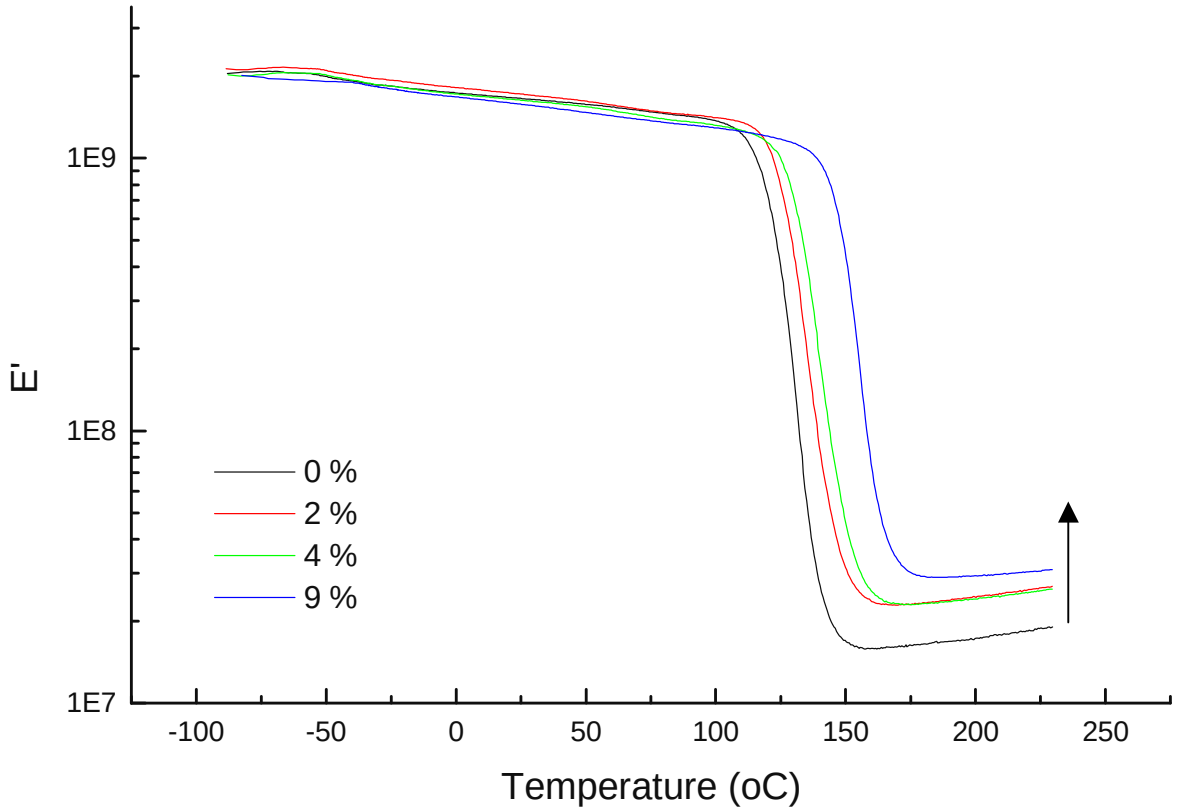


# DMTA – cure agent effects




Curing agent can influence the nature of the dispersion

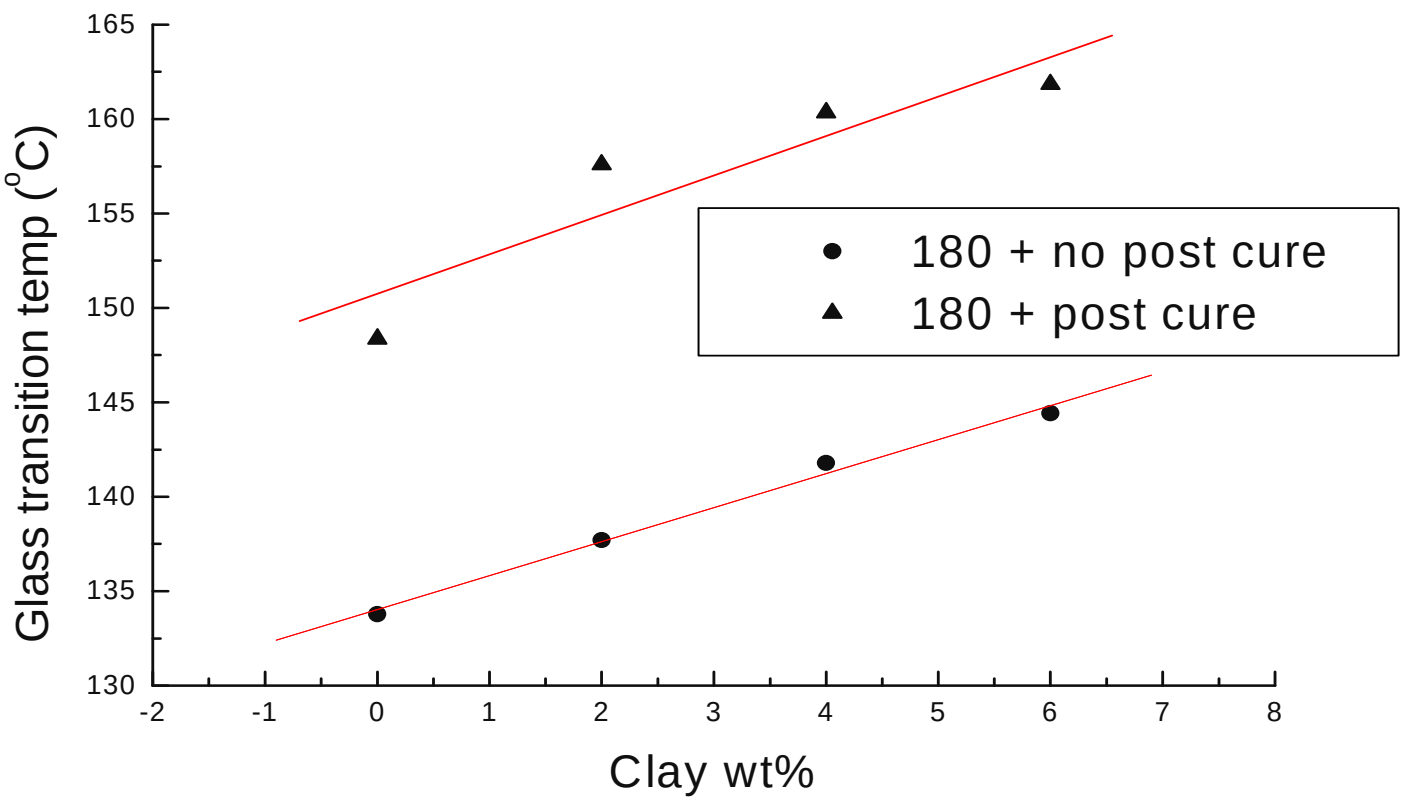
# Dynamic Mechanical Thermal Analysis




Addition of clay

Addition of clay increases the temperature at which the material softens and its high temperature strength.

# Glass transition




Enhanced mechanical properties are being displayed allowing the resins to be used in more extreme conditions

# Conclusions

- Through the addition of clay nanocomposites it is possible to enhance
  - glass transition temperature and modulus
  - thermal stability of the epoxy.
- The dispersion of clay and the choice of cure conditions are critical to maximise these improvements
- These improvements could lead to cheaper, stronger and more heat resistant coatings for the aerospace industry.

# Task 2 – Environmentally Friendly Flexible Foams

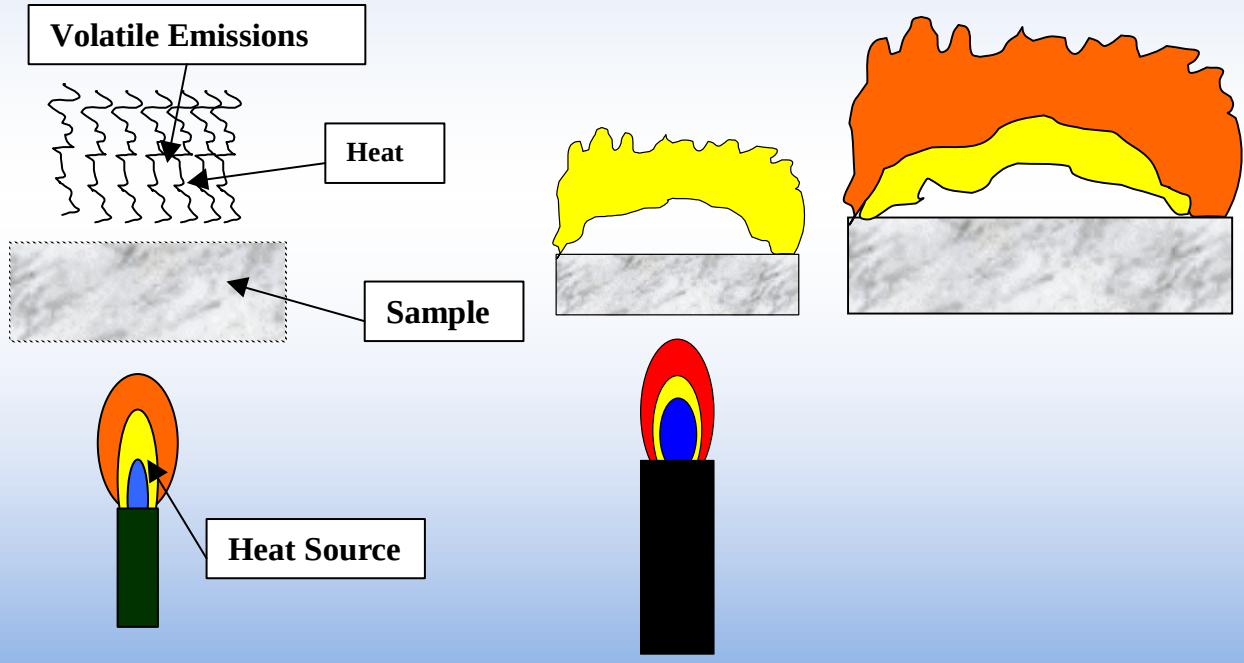
## Environmentally Friendly Flexible Foams

Target:-

- Eliminate the use of halogen containing organic fire retardant additives.
- Match the properties of the current commercial fire retardant flexible foams.

# 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.

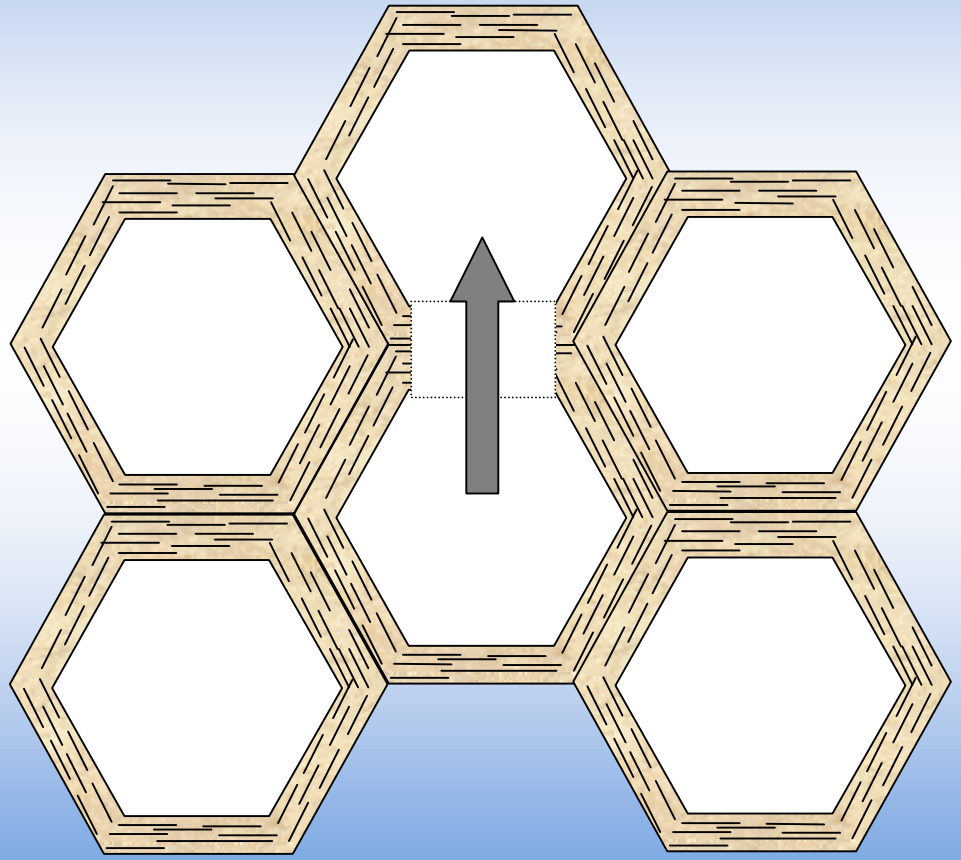



**Precombustion - - Initiation of combustion - - Self sustained combustion**

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

# Strathclyde approach to flame retardancy in polymer foams.

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

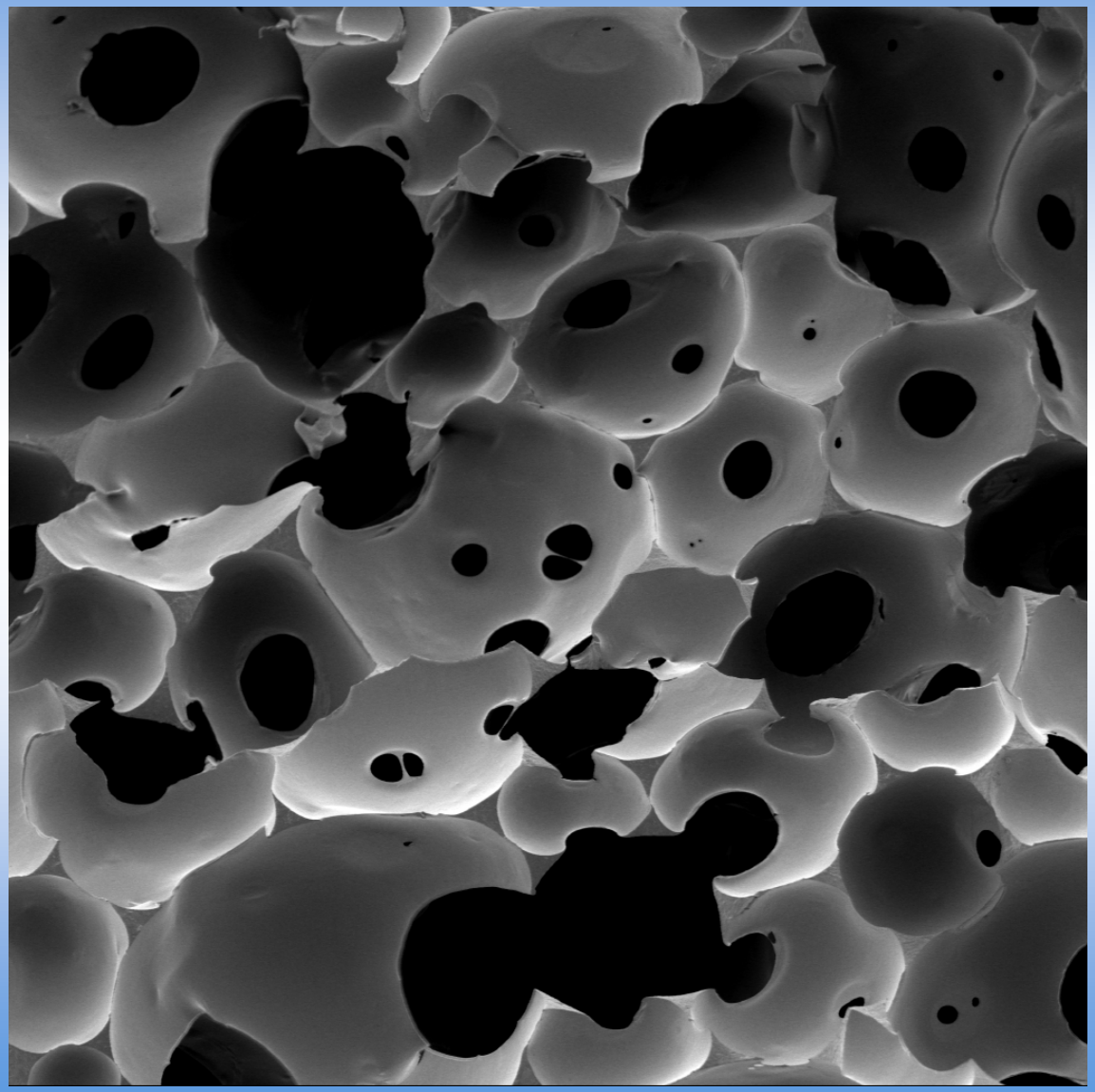


# Flexible Foam Systems

- A series of flexible foam system have been produced with the required flexibility and incorporating nanocomposite organically modified clay materials.

{These systems have been patented}

# Electron Micrograph of PU foam



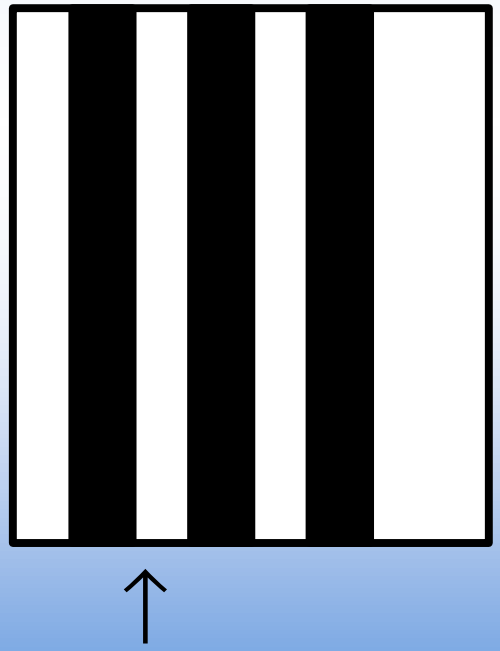
# Molecular Nano composites

- These are useful where anisotropic properties are required in a polymer material.
- Example:- styrene-butadiene- styrene triblock copolymer
- At room temperature
- Styrene is a hard glass modulus ~$10^{9}$ $Nm^{-2}$
- Butadiene is a rubber modulus ~$10^{6}$ $Nm^{-2.}$

# Triblock copolymers

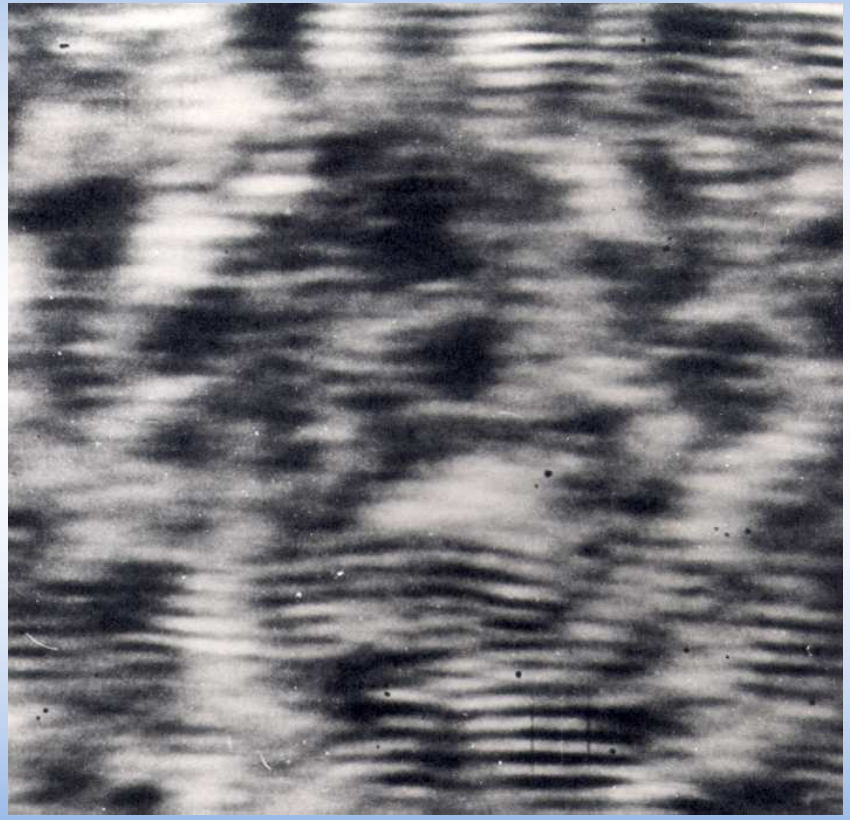
- These materials can phase separate and in extrusion will flow align to give anisotropic materials

low modulus →

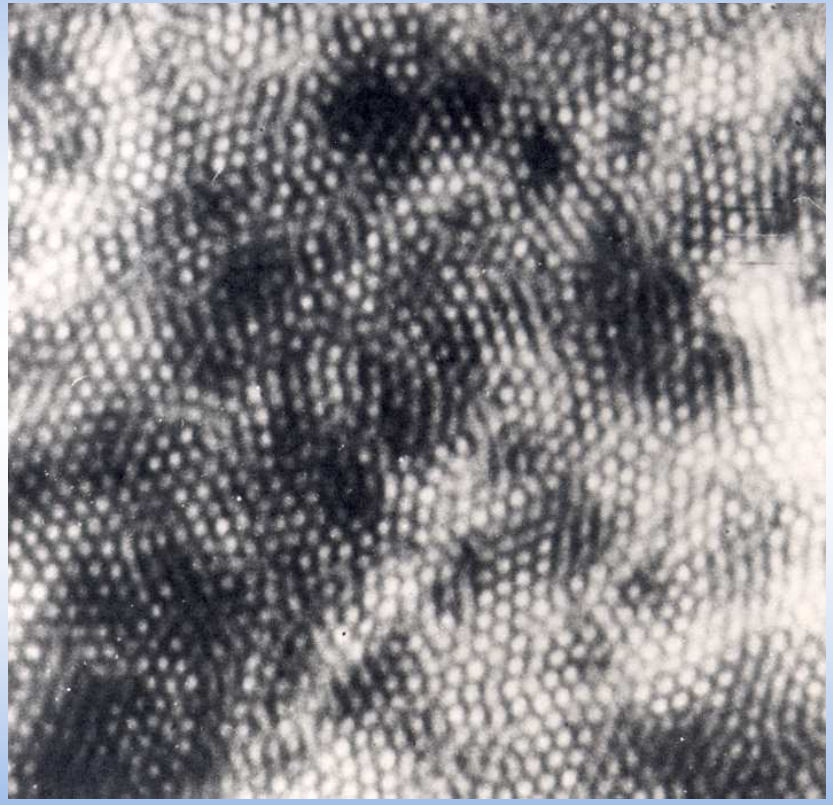


↑ high modulus

# Electron Micrographs of Styrene-Butadiene -Styrene



Parallel to draw direction



Perpendicular to draw direction

# Application

- These materials are used to create matrix materials which have anisotropic characteristics and commercial applications.

# 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.

# Acknowledgements


- Dr J.J. Liggat, Dr John Daly,
- Dr Ian Rhoney, Dr Sharon Ingram,
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- Scottish Enterprise.
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# Thank you for listening

Any Questions?