Structure-property relations in polymer nanoclay composites

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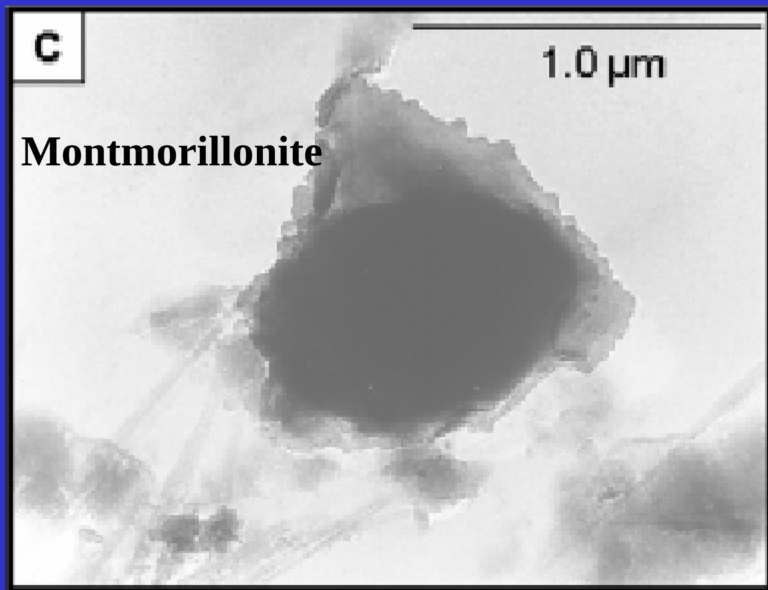
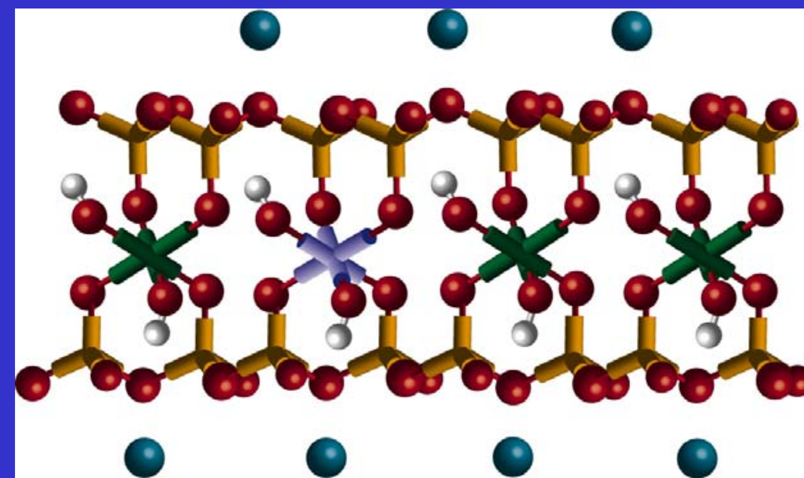
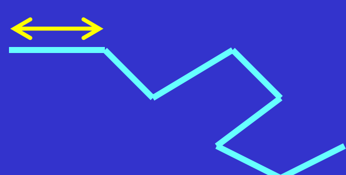
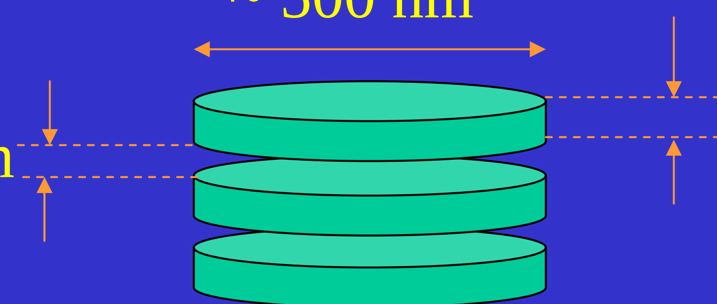
Nanoclays



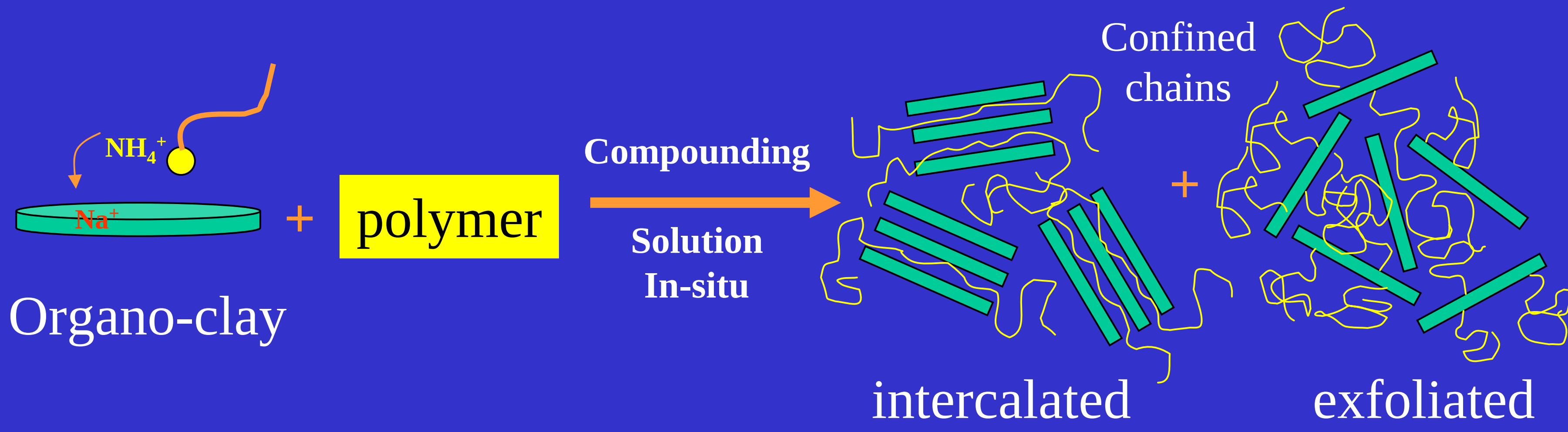


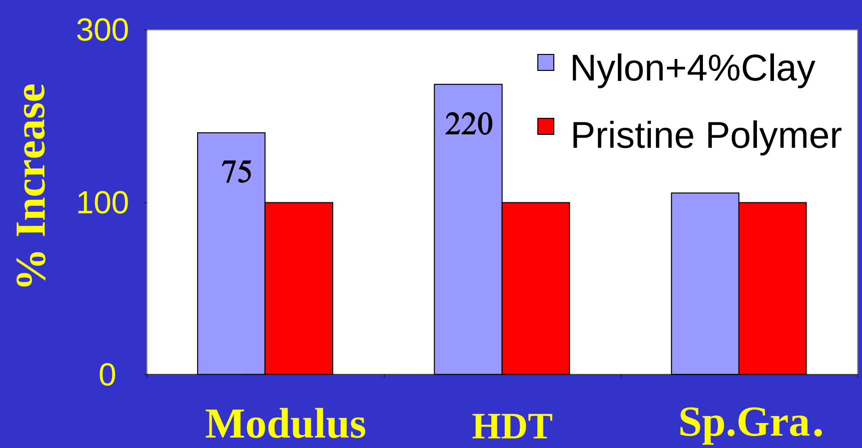
$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$

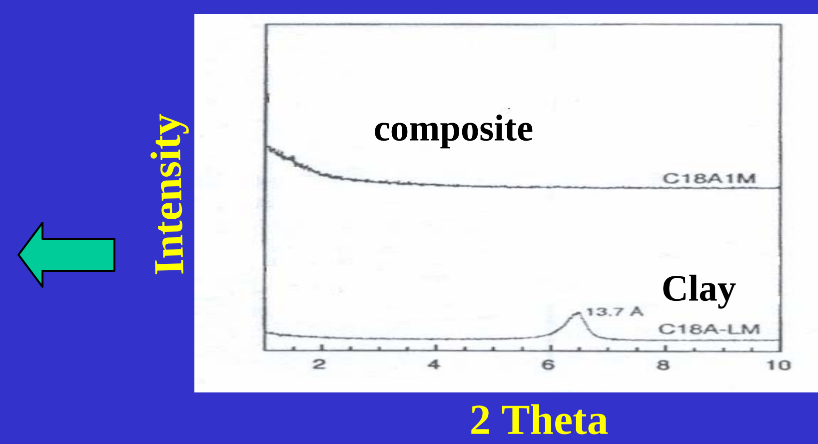




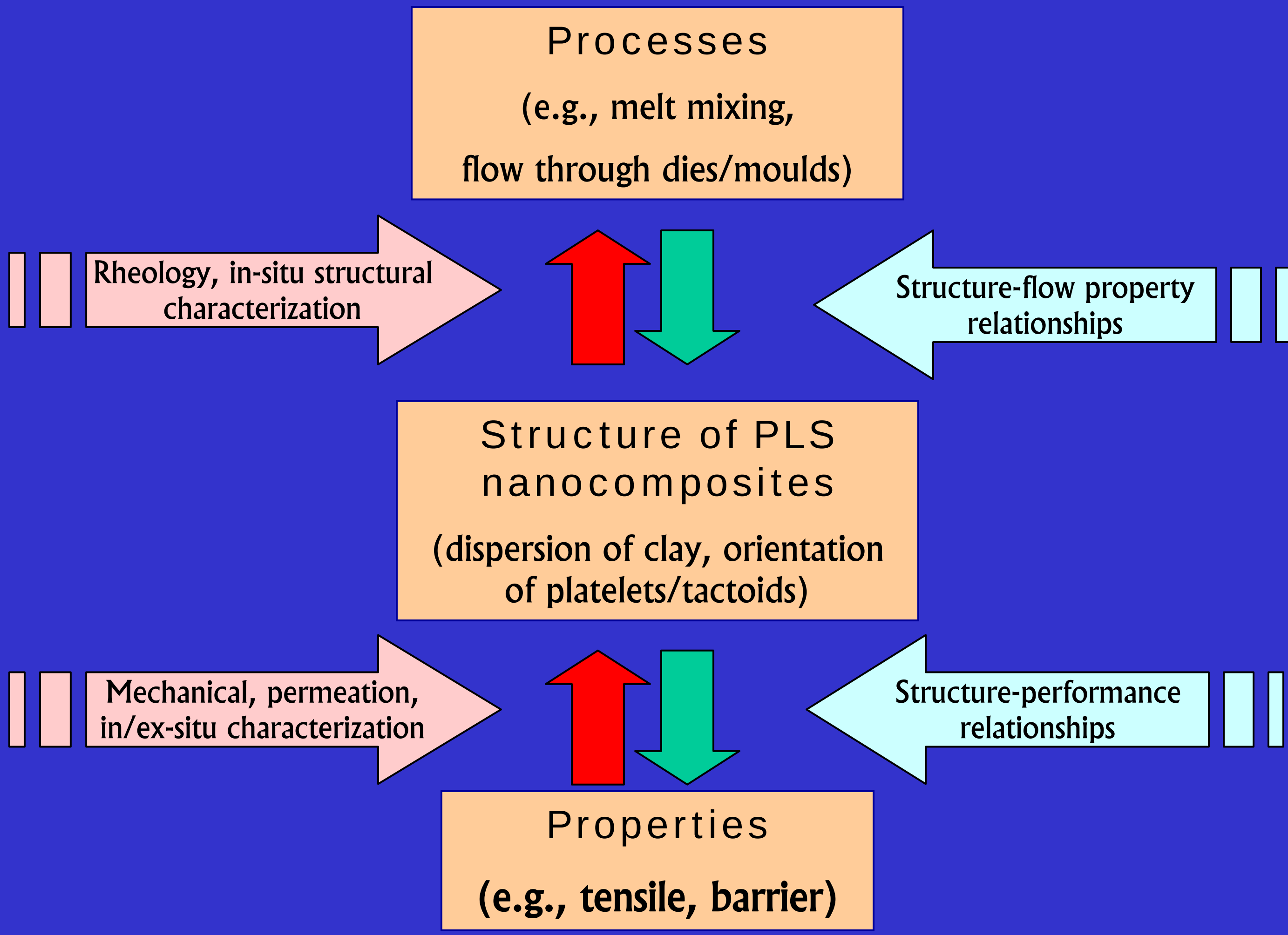
Polymer nanoclay composites







Structure-property linkages



Materials & methods

Materials:

1. sPP (Fina Oil & Chemical Co., M_w=87,000, M_n=25,588)
2. Montmorillonite (Southern Clay: C20A; DMDH-tallow)
3. Compatibilizer: iPP-g-MAH (M_w=122700 & M_n=44800 (PS), MAH:1wt%)

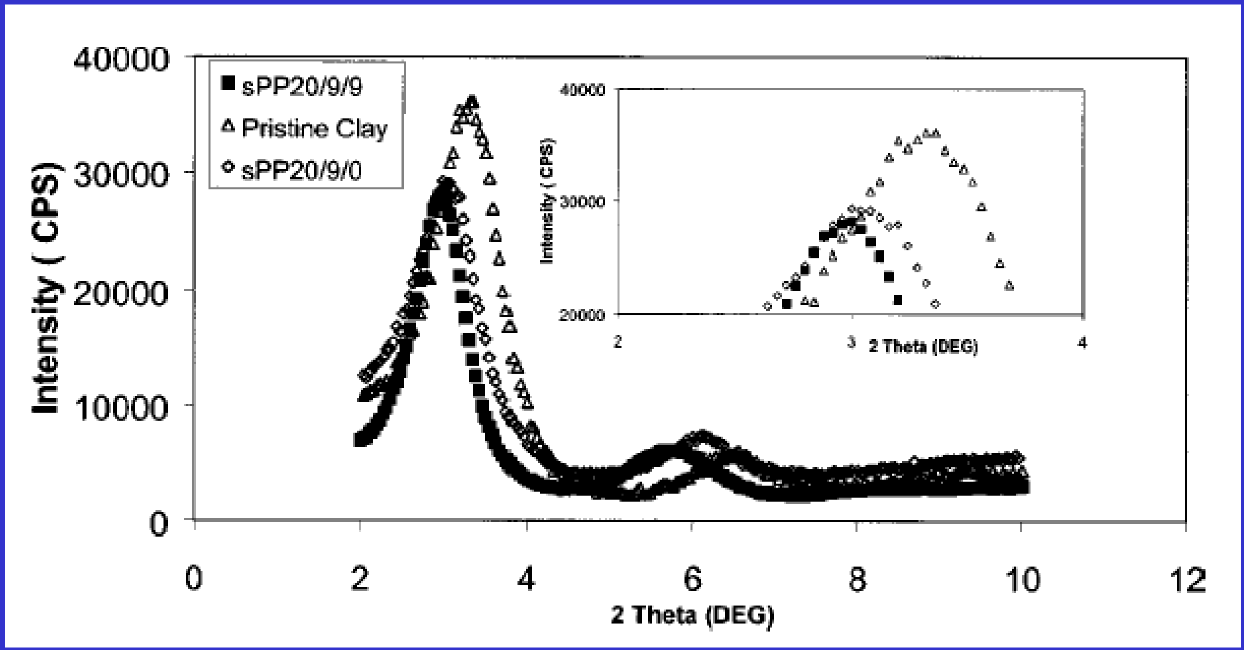
Compositions:

1. Clay loading: 3 – 9 wt%
2. Compatibilizer: equivalent amount to clay loading
3. Nomenclature: sPP(MFI)/clay wt%/compatibilizer wt%

Methods:

1. Synthesis: melt compounding (ZE-25 TSE; T=140 – 190^{o}C)
2. Microstructure: XRD
3. Rheology: controlled stress (Bohlin CVO-50), controlled strain (ARES)
4. Processing: Rheo-XRD (Cambridge-MPR), tape extrusion (Capillary rheometer)
5. Property: Tensile testing on UTM (Instron 4204)

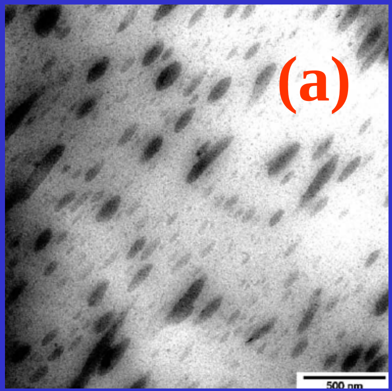
Microstructure

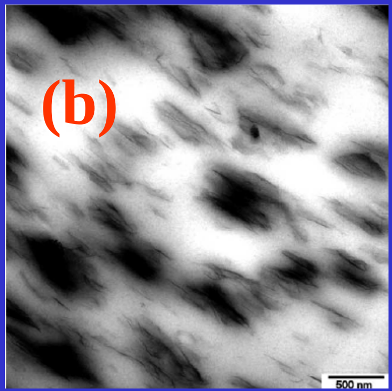


(a): sPP+compatibilizer

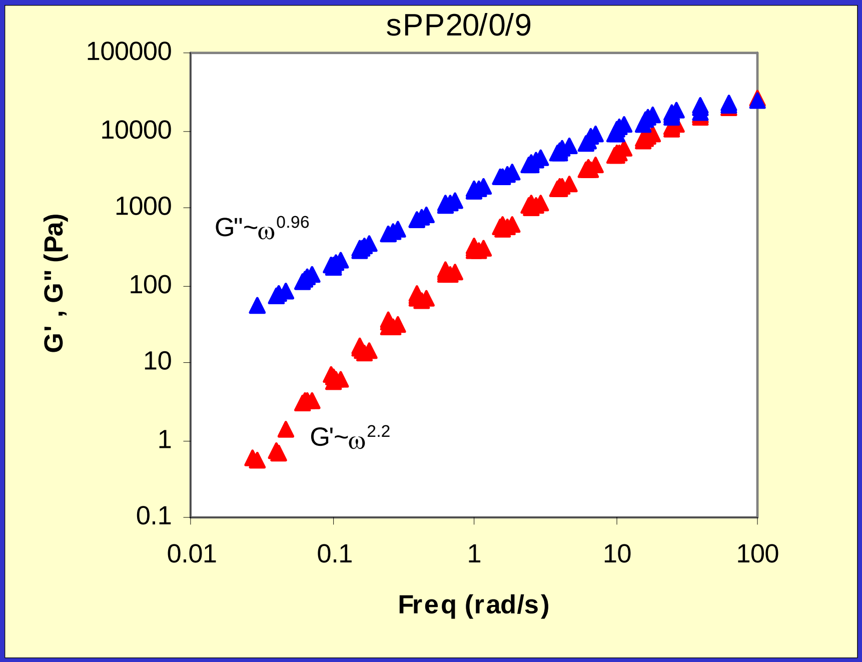
(b) sPP+clay+compatibilizer

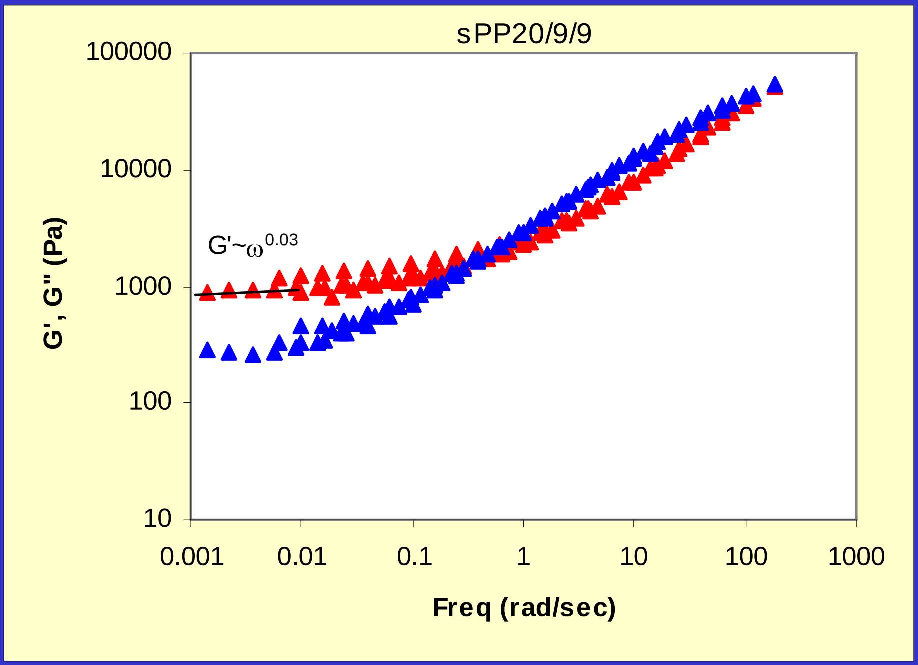
(Kaempfer et al., Polymer 43 (2002) 2909-2916)





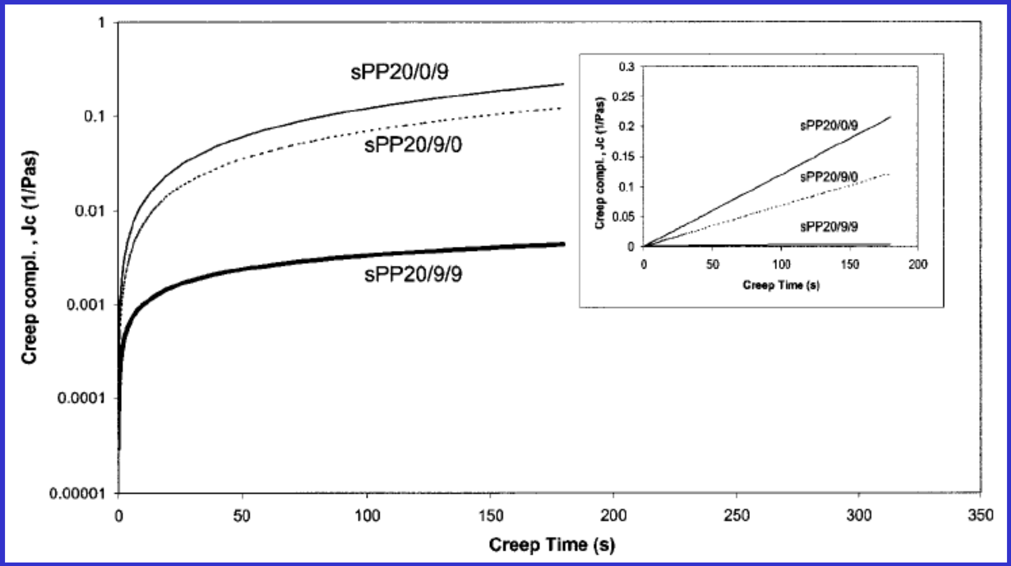
Linear rheology





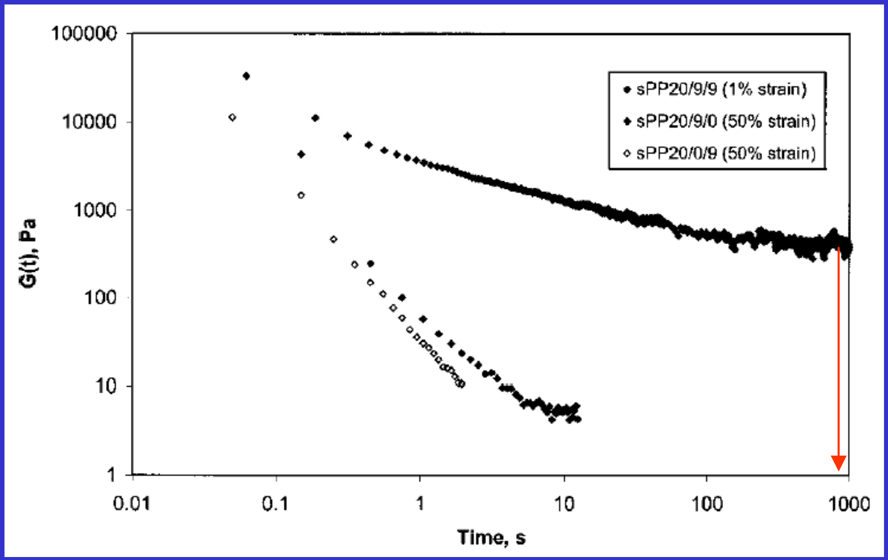
- ΔE_a ~ 38 kJ/mol for matrix polymer & hybrids
- No effects of confinement
- Solid-like response

Linear rheology



Creep experiments show a Newtonian response at zero shear

Stress relaxes over time scales ~ 1000 s for compatibilized hybrids.

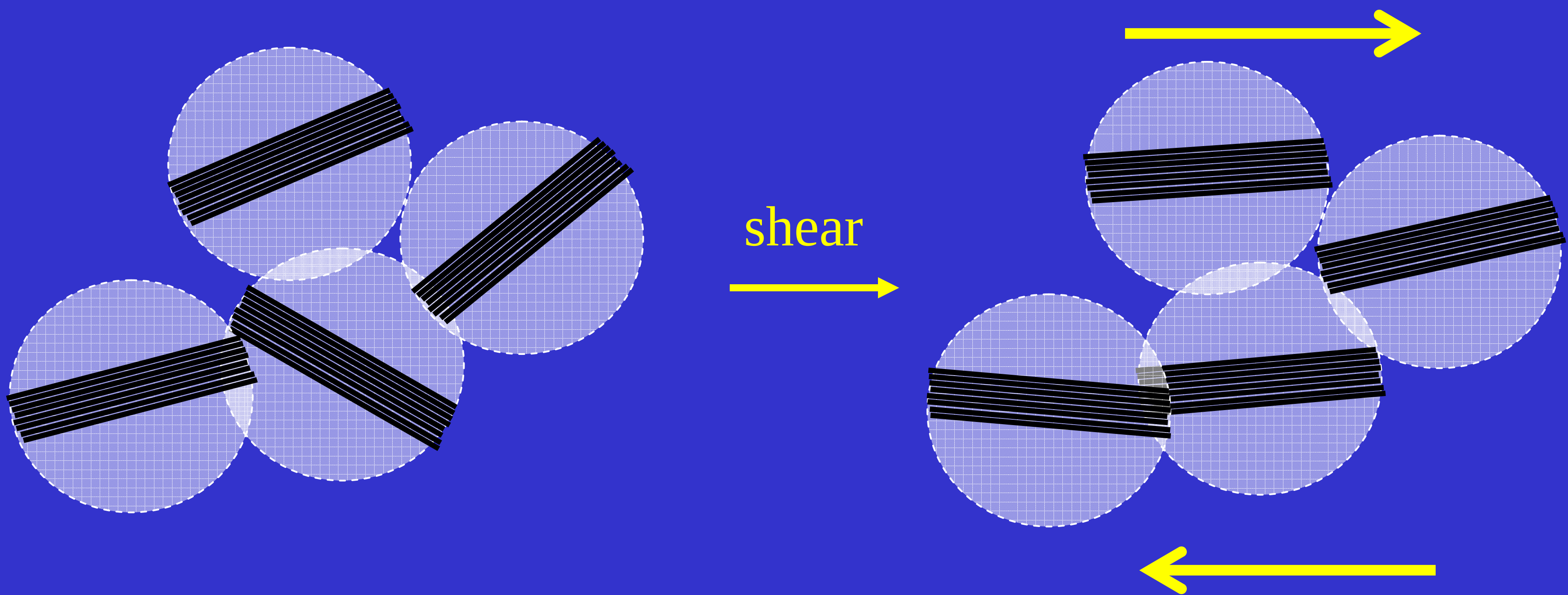


Rheological story…

Molten nanoclay composites exhibit

- solid-like behaviour at low strains
- have high zero-shear viscosity
- no effects of chain confiment
- very slow (~ 1000 s) stress relaxation

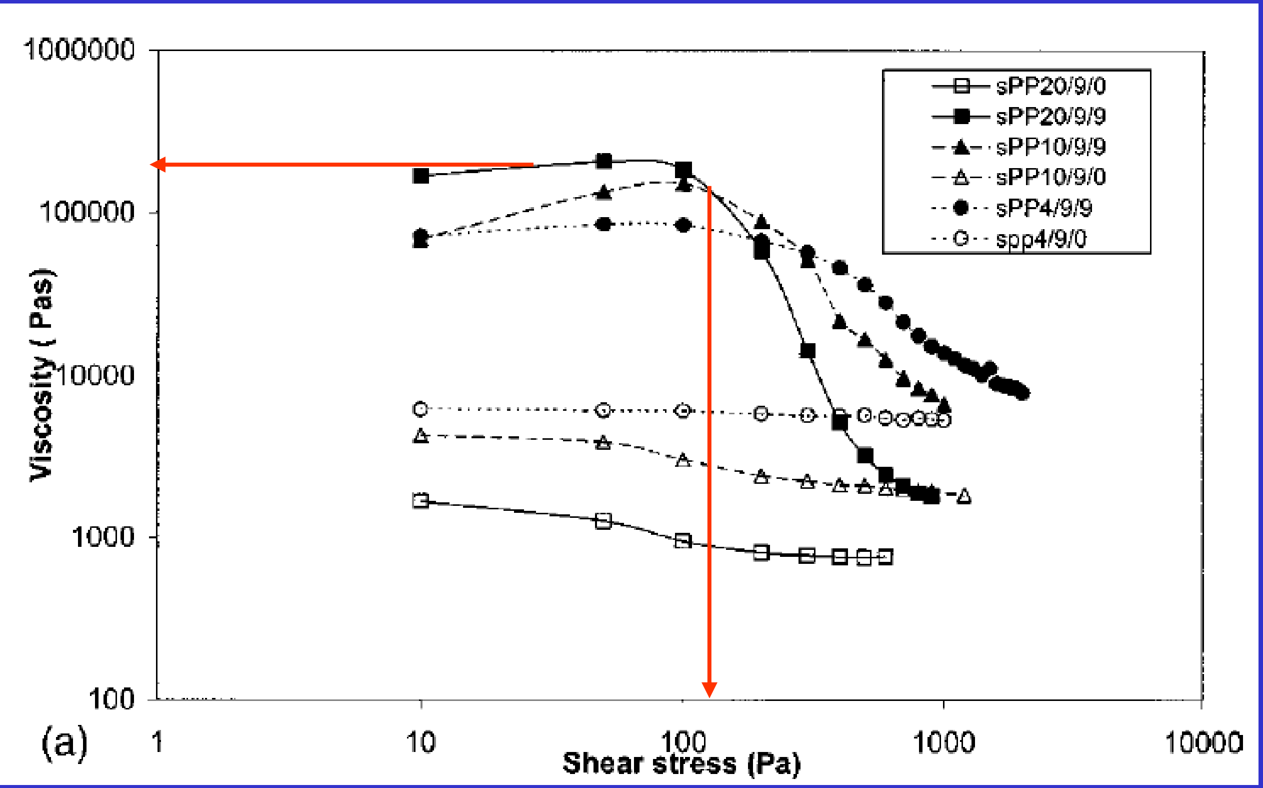
Linear → Non-linear



A percolating network

Flow alignment ?

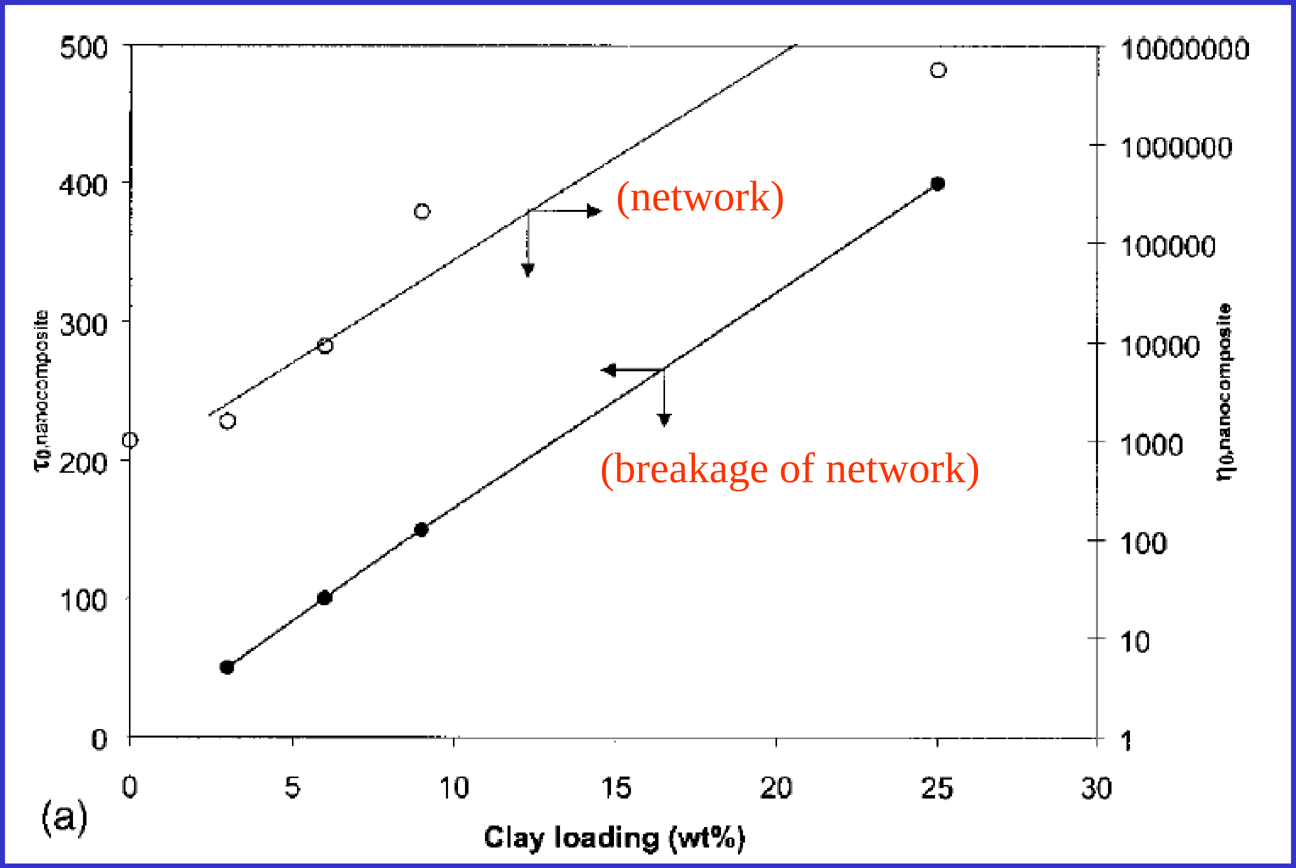
Non-linear rheology



$\lambda \sim \eta_o/\tau_o = 1000$ s

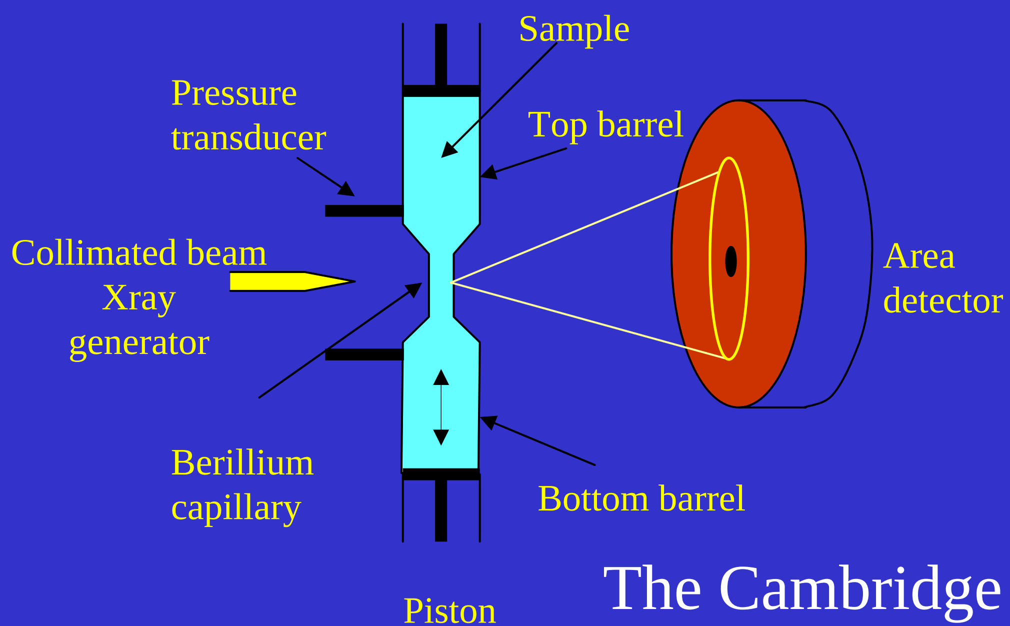
Cox-Merz fails

Non-linear rheology

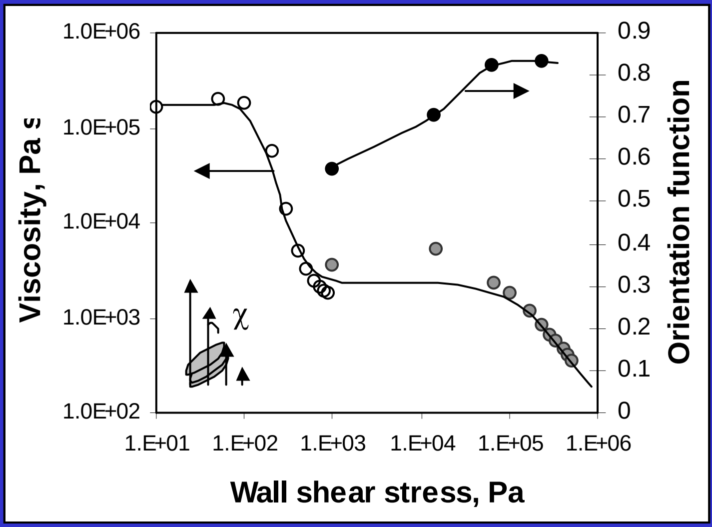


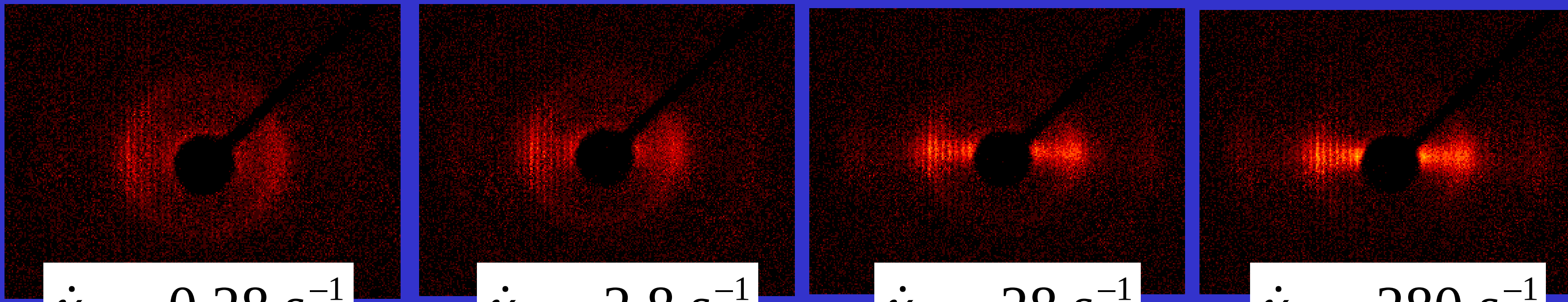
Rheology…….. An indirect evidence of orientation

Rheo-XRD: Direct orientation measurement



The Cambridge MPR





$\dot{\gamma}_w = 0.28\ s^{-1}$ $\dot{\gamma}_w = 2.8\ s^{-1}$ $\dot{\gamma}_w = 28\ s^{-1}$ $\dot{\gamma}_w = 280\ s^{-1}$

Relaxation of orientation

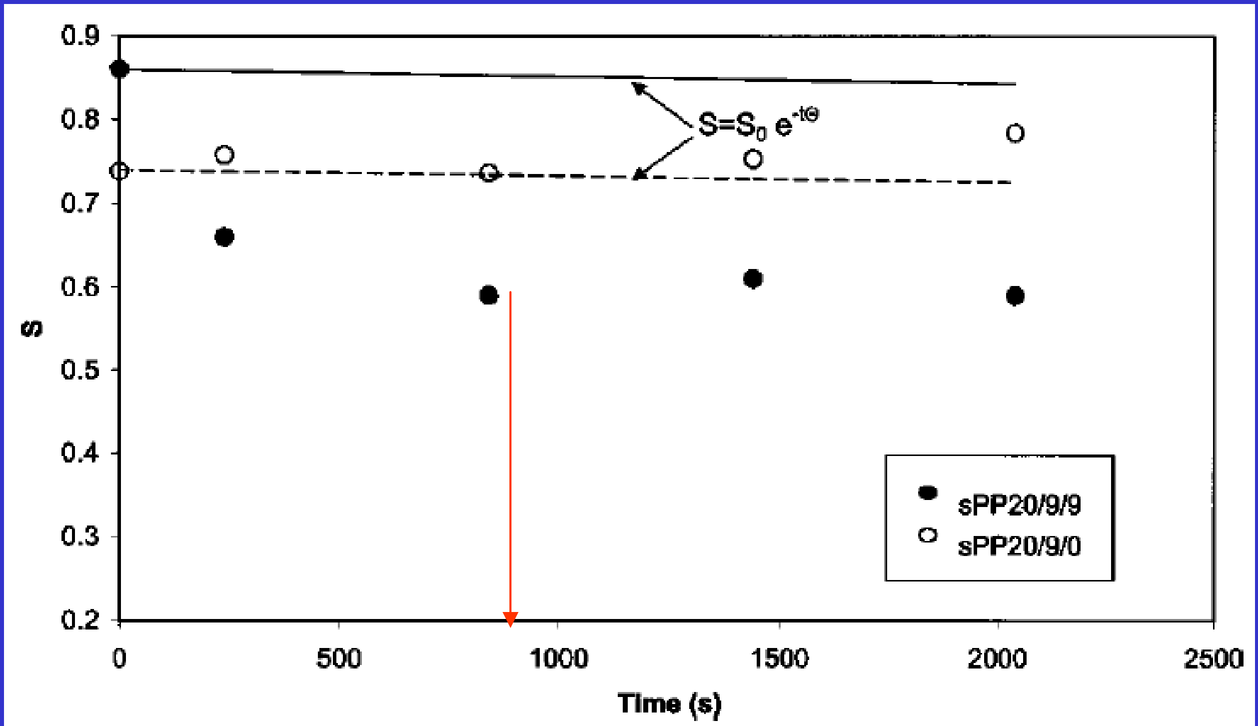
$$S = S_0 \exp(-t/\Theta)$$

where,

$$\Theta = \frac{3kT}{16\pi\eta_{\text{matrix}}a^3}\left[2\ln\left(\frac{2a}{b}\right)-1\right].$$

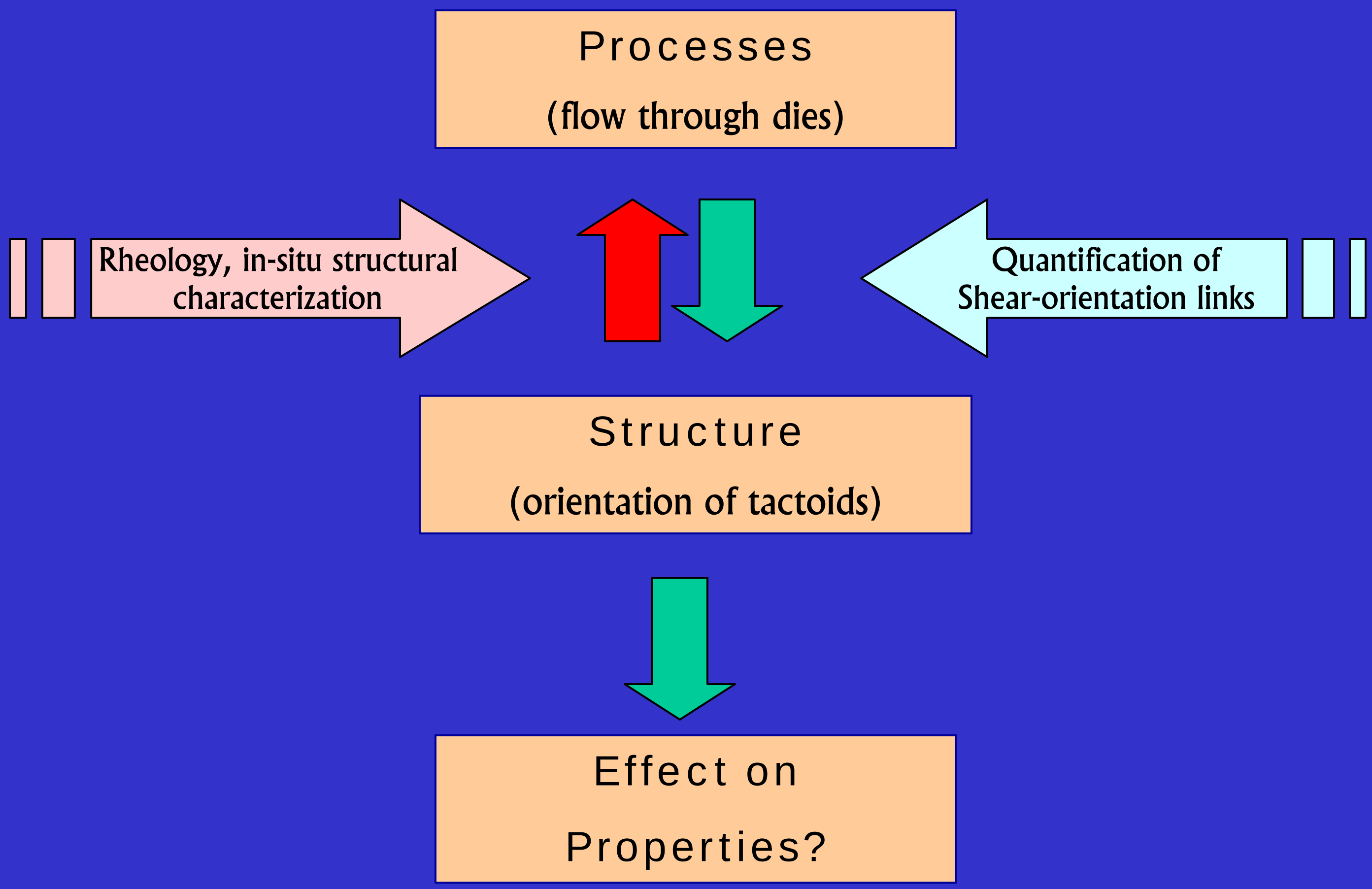
For a=500 nm, b=30nm & ho=800 Pa s

$$\Theta \sim 10^{-6}\ s^{-1}$$

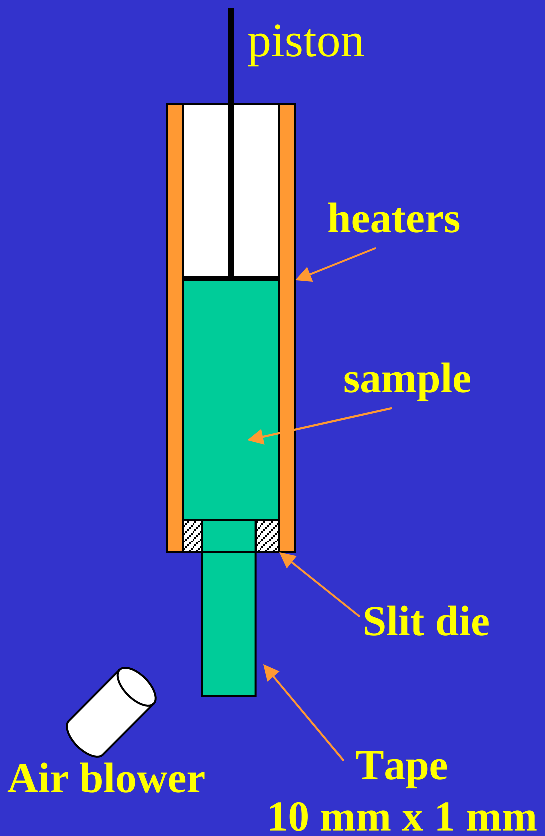


Rapid relaxation perhaps caused by stress transfer from melt to tactoids
Orientation relaxation time ~ 1000s → matches with the rheological time

The story so far……



Tape extrusion: clay orientation - modulus



Tape samples

σ_w=6x10^3 – 1x10^5 Pa

T=190^{o}C

1D XRD

(Rigaku, CuKα, goniometer)

platelets/tactoid

2D XRD

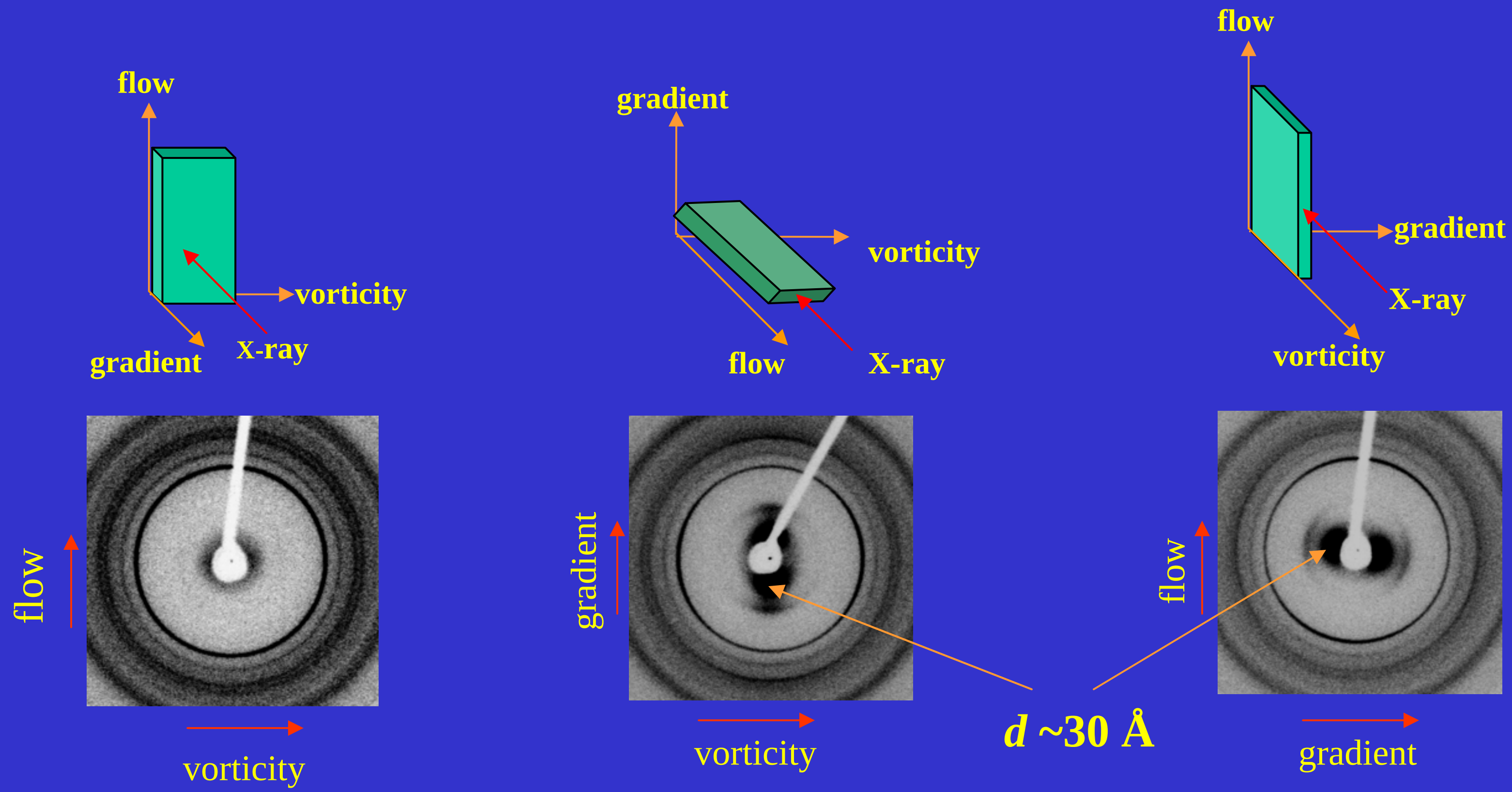
(Rigaku, CuKα, image plate)

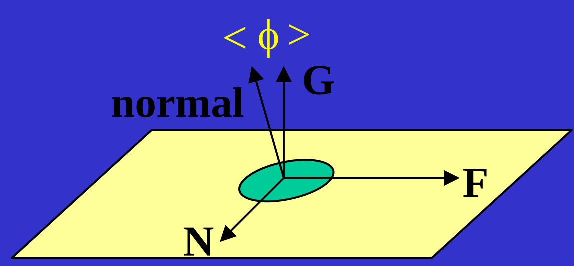
Orientation measurement

Tensile testing

(Instron UTM, 25mm/min)

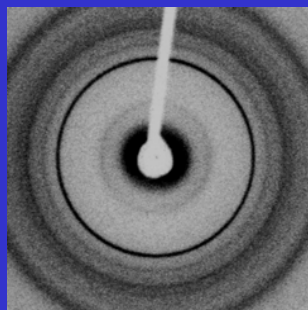
Clay orientation in tapes



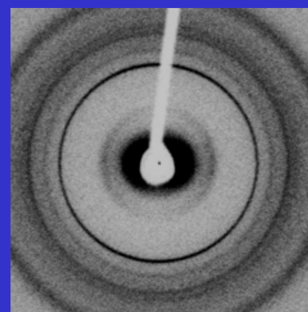


Clay orientation with shear

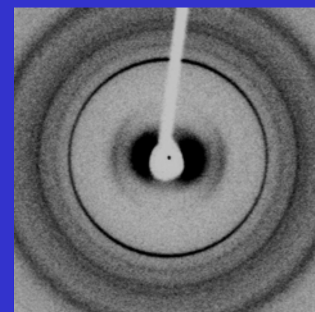
V_p = 0.01 mm/s



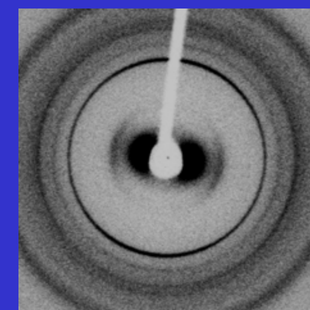
V_p = 0.05 mm/s



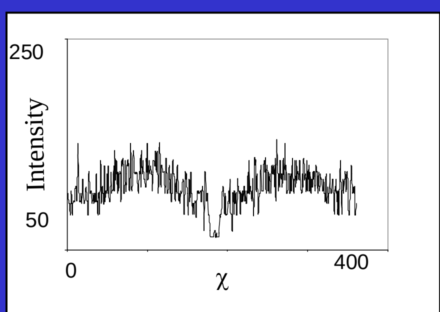
V_p = 0.9 mm/s



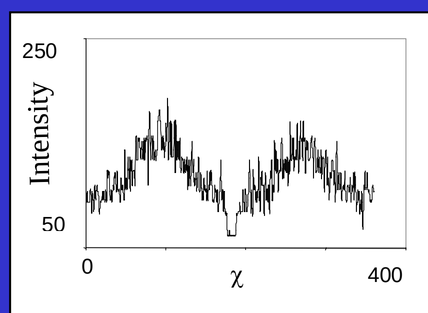
V_p = 1.5 mm/s



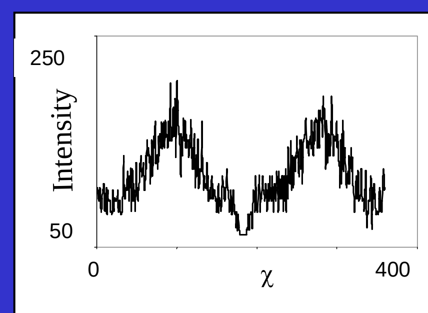
X-rays along Neutral (or vorticity) direction



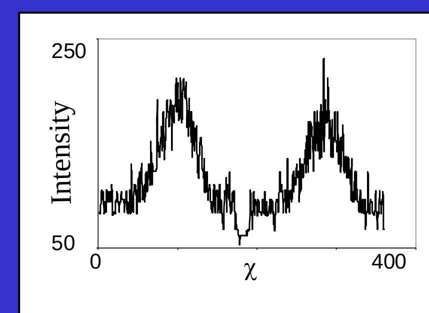
S=0.15



S=0.16

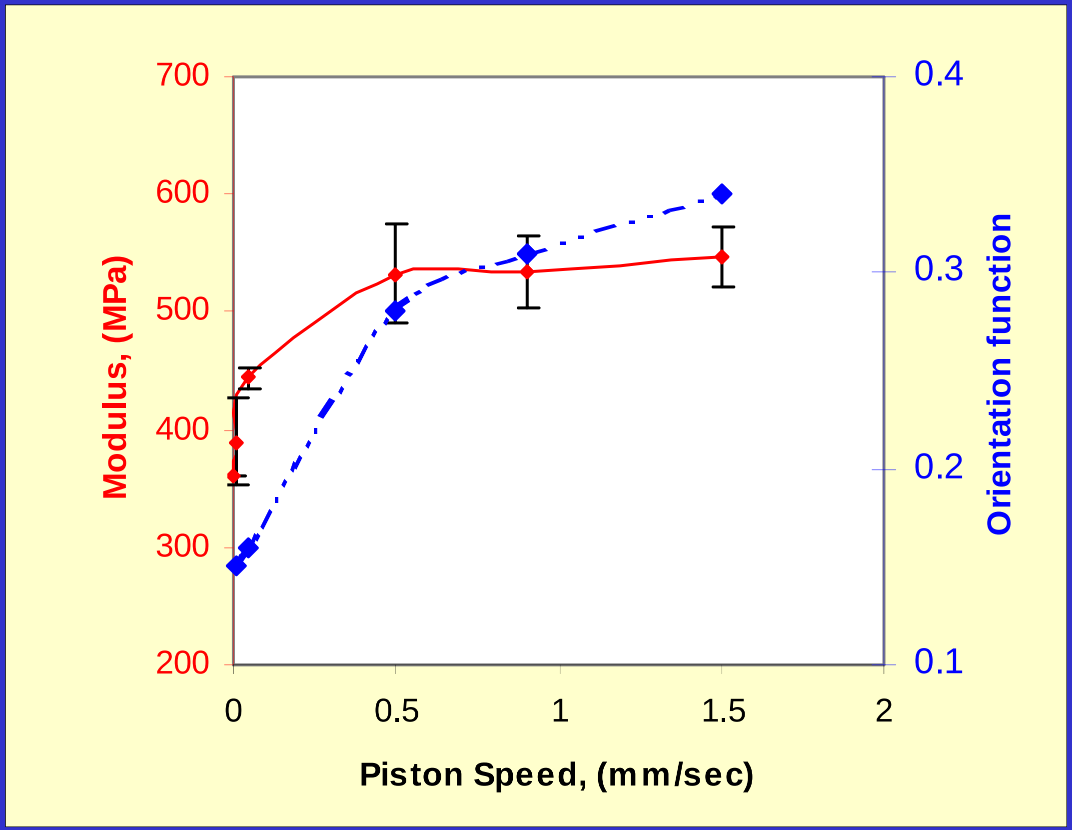


S=0.31



S=0.33

Modulus – clay orientation



Prediction of modulus:

Halpin-Tsai eqn:

$$\frac{E_{composite}}{E_{matrix}} = \frac{1+2A'\eta'\phi'}{1-\eta'\phi'}\eta_\theta$$

Here, (Brune et al., 2003)

$$A' = \frac{A}{\hat{N}}\left(\frac{1}{1+(1-1/\hat{N}\frac{s}{t}}\right)$$

$$\eta' = \frac{E'_r - 1}{E'_r + 2A'_f}$$

$$\phi' = \phi\left[1+\left(1-1/\hat{N}\right)\frac{s}{t}\right]$$

$$E'_r = E_r\left(\frac{1}{1+(1-\hat{N})\frac{s}{t}}\right) + \frac{(1-1/\hat{N})\frac{s}{t}}{1+(1-1/\hat{N})\frac{s}{t}}$$

$$\hat{N} = N + (1-N)\left(\frac{s}{t}\right)\left(\frac{\phi}{1-\phi}\right)$$

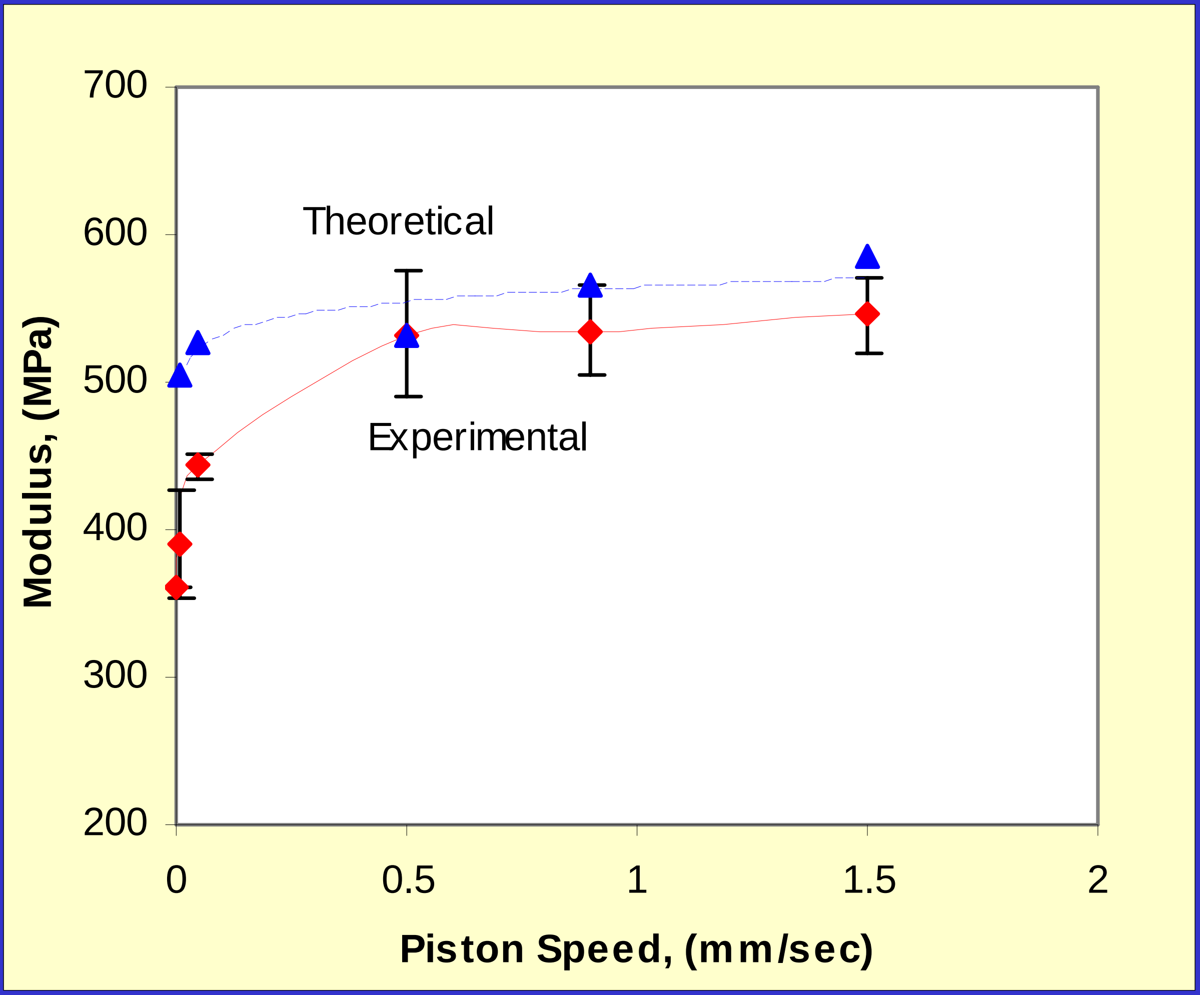
$$\eta_\theta = \int_0^{\pi/2} f(\theta)\cos^4\theta \, d\theta$$

where, $f(\theta)$ = fraction of tactoids oriented within θ & $\theta + \mathrm{d}\theta$

We assume that

$$f(\theta) = \frac{I(\theta)}{\int_0^{\pi/2} I(\theta)d\theta}$$

Predictions



Conclusions