Polymers Multiscale Properties

1st IAG mtg NPL

6September 2006

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Exploitation # 1

- Properties vs Performance
  - Either

$$P \quad \text{or} \quad \frac{P^n}{\rho \times (Cv+Cp)}$$

Where P = property, ρ = density &

Cv = material cost per unit volume

Cp = material cost of processing

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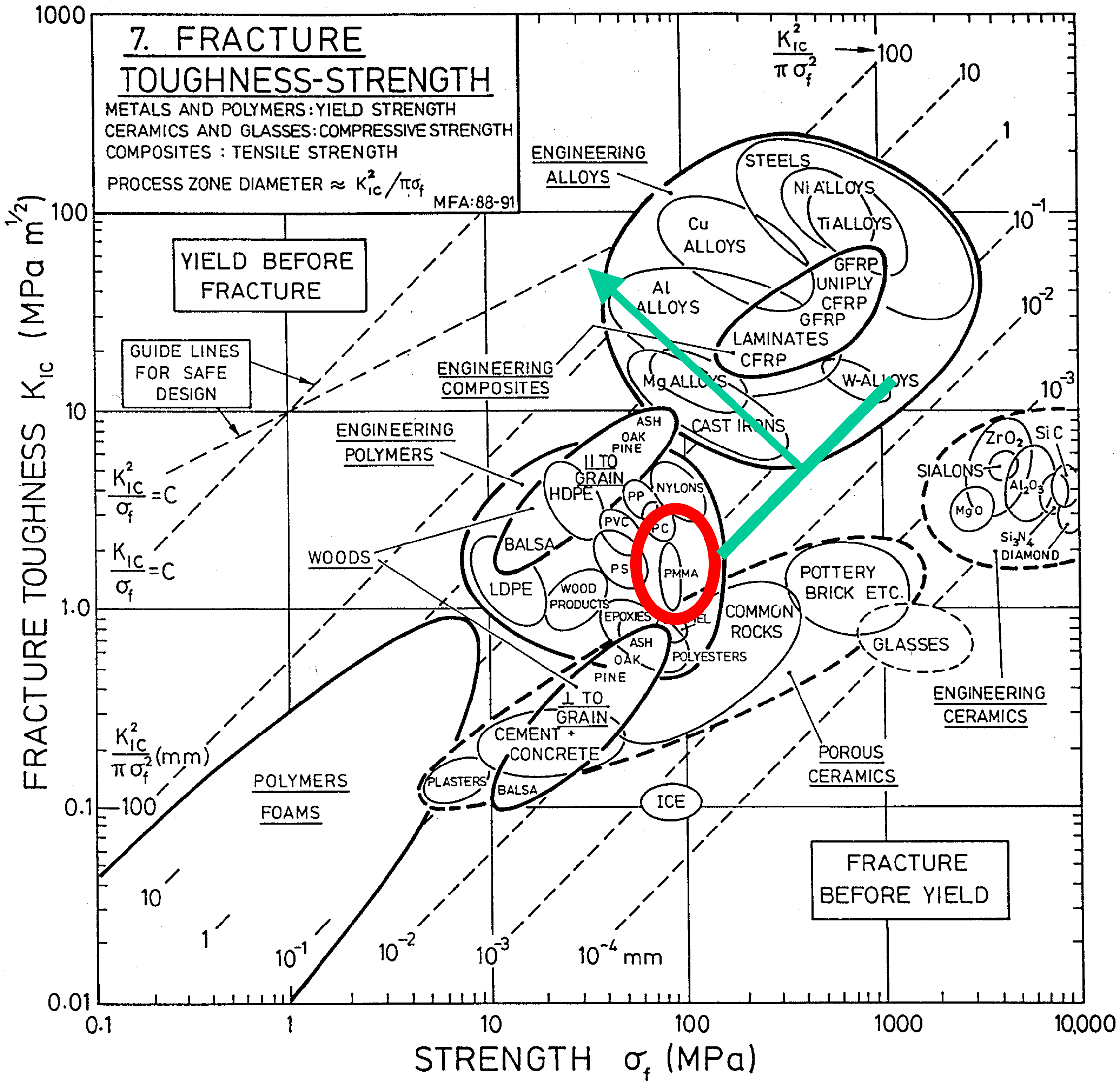
Ashby - Materials Selection in Mechanical Design



PMMA

Materials Property ratio of importance

$(K_c / \sigma_y)^2$

Materials Selection in Mechanical Design
MF Ashby
Butterworth Heinemann (1992)

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The World of Composite Materials

Composites vs Nanocomposites

- How do Composites work?
  - Enhancing material properties by including stiffer/ stronger materials into the polymer
    - Requires good interface chemistry to couple the phases together
    - Best behaviour seen with either full orientation, or with random distributed/dispersed mixing
    - Fillers do not alter bulk behaviour of polymer chains (eg thermal transitions, crazing) but can enhance certain desired behaviours (eg crack tip blunting / toughness)
    - Properties are highly predictable, using rule of mixtures approach, based on volume fraction of fillers
    - Nanoscale fillers (eg impact modifiers) also follow rule of mixtures

Composites vs Nanocomposites

- How do Nanocomposites work?

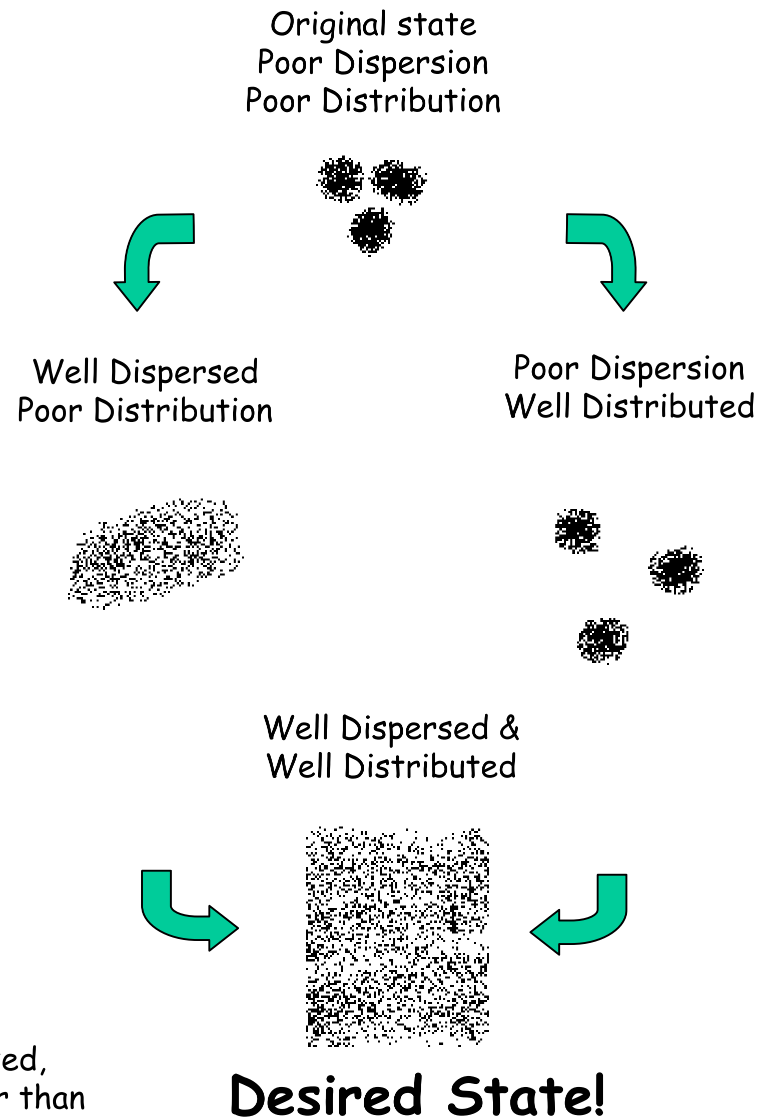
  - Enhancing material properties by including nanoscale materials into the polymer (eg clays/silicates/carbon nanotubes).

  - Requires favourable thermodynamics to achieve nanodispersion at molecular level (exfoliation is desired state)

  - Acts by achieving local chain topological constraints – suppression of free volume

  - The local and global dynamic behaviour of the polymer chains in nanocomposites are markedly different from the bulk

Distributive vs Dispersive Mixing with traditional fillers



Dispersive Mixing

Controlled by Shear Stress, not Strain

Good Mixing achieved with particles of similar size at high viscosity

Force to break particles
$F_{max} = 3\pi \eta\gamma (r_1 r_2)$

η = viscosity
γ = strain rate
r_1, r_2 are radii of particles 1,2

Energy dissipated / unit volume

$U = F^2 / (9\pi^2 r_1^2 r_2^2 \eta)$

Improve by high viscosity & particles of approximately same initial size. Predicts if force is fixed, then cannot break particles smaller than
$r_1 r_2 = F_{max} / 3\pi \eta\gamma$

Distributive Mixing

Controlled by Strain, not Shear Stress

Good Mixing achieved in Turbulent flow (Re > 2000)

$Re = D v \rho / \eta$

D = Diameter
v = velocity
ρ = density
η = viscosity

Mixing index (A/Ao) is related directly to strain, γ

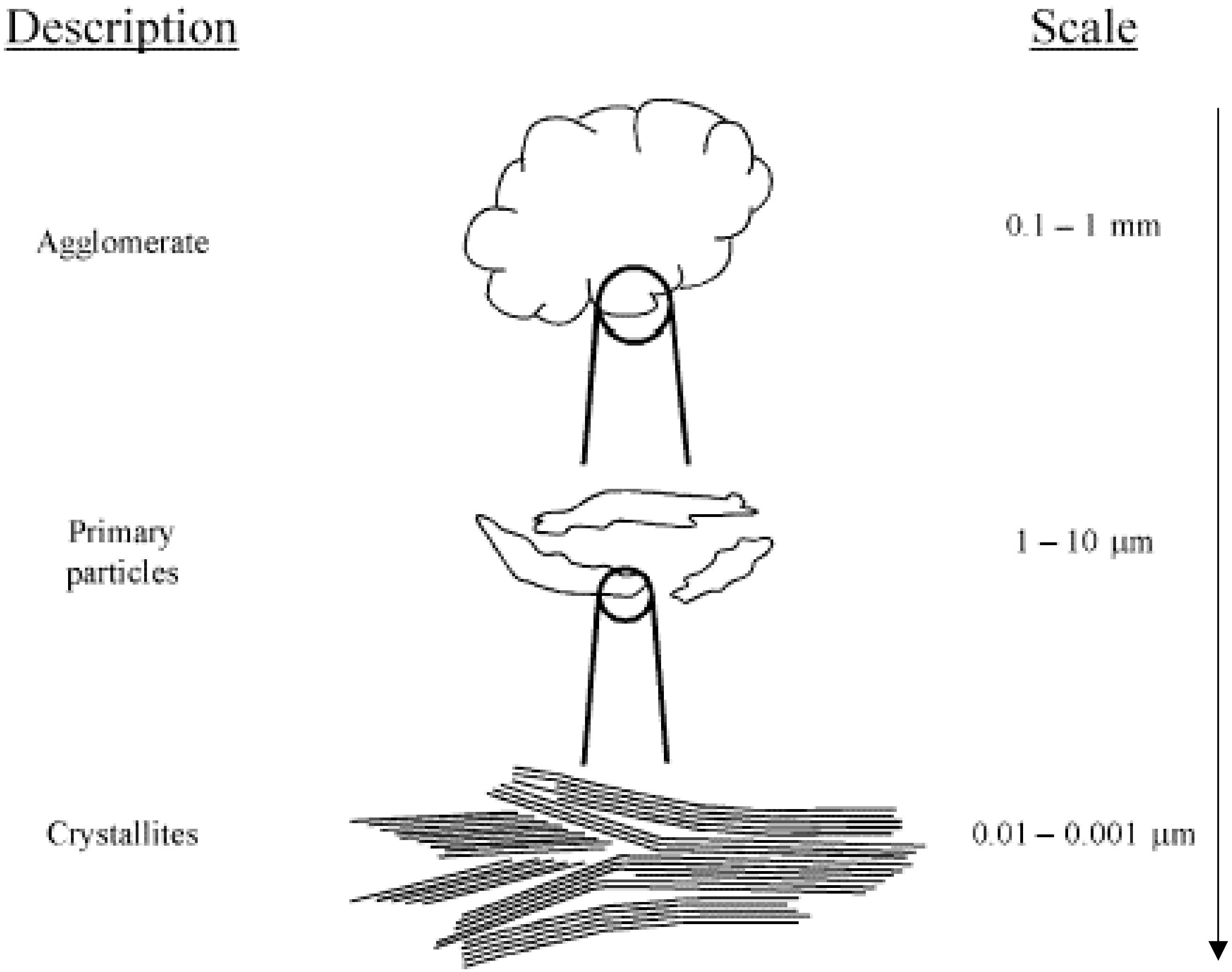
Improve by interrupting flow and realigning continuously to high high strain

Note Mixing Index (A/Ao) = (Do/D) ie ratio of diameters

Composites vs Nanocomposites

- Benefits of Nanocomposites
  - Main thermal transition (Tg) in polymer suppressed (entirely in some systems by some measures!)
  - Local chain orientation enhanced , hence modulus increased
    - Some work report increase in toughness/strength, others report decrease
    - Can improve abrasion resistance
  - Rheological behaviour altered
    - Generally stiffer, with onset of shear thinning at reduced frequency. This implies some change to reptation behaviour?
  - Fire behaviour enhanced
    - Fillers can significantly reduced rate of heat release, but tend to leave time to ignition unaltered. May be due to chemical composition of filler (eg contain O_2)
  - Barrier properties enhanced
    - Nanofillers extend mean free path length (tortuosity) for penetrants and suppresses diffusion process
  - If exfoliated, optical properties remain unaltered from bulk polymer

Nanoparticle Structure

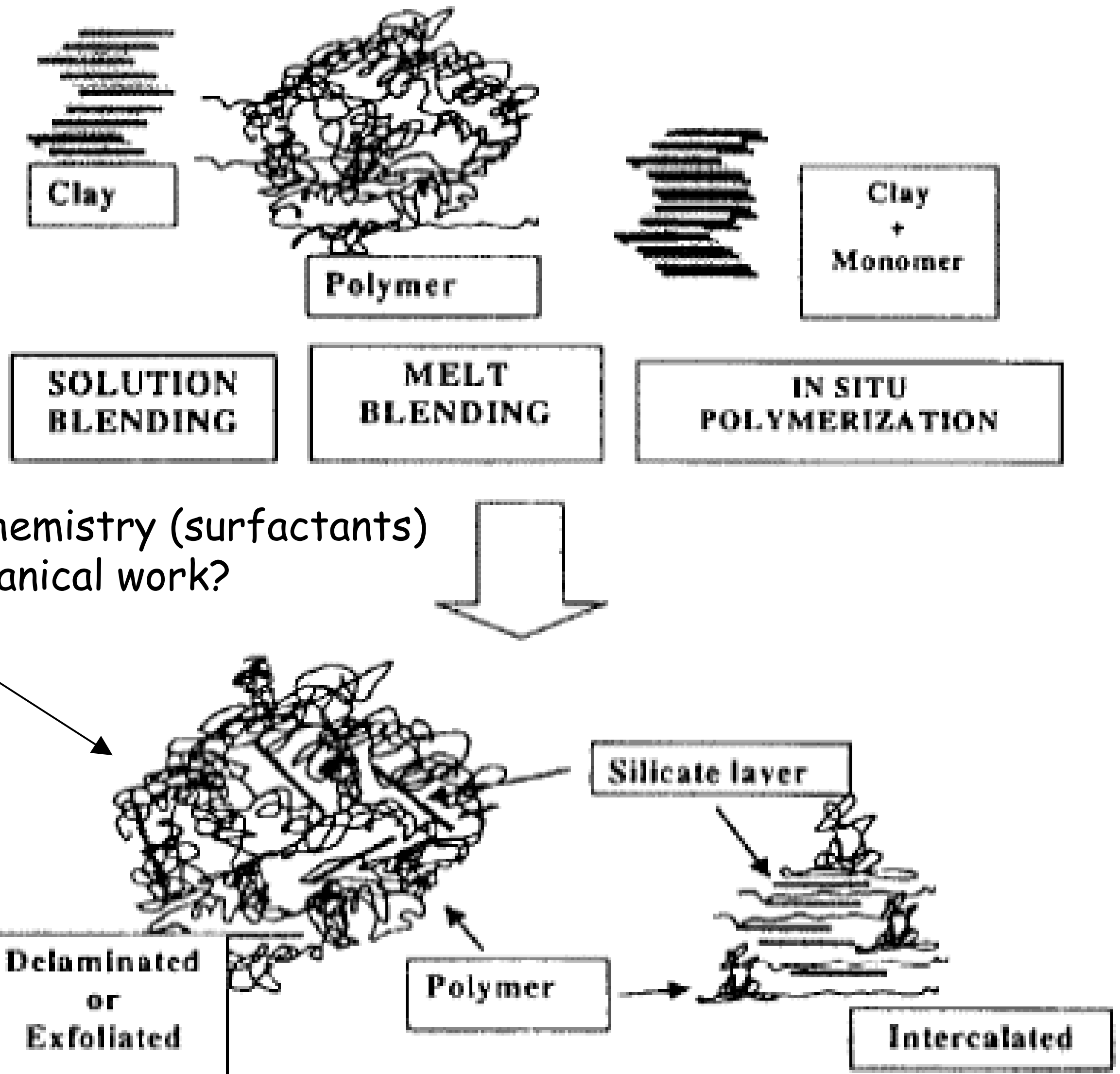


Exfoliation
only achieved in
polymer if this
structure can be
broken down to
Nanoscale

Enhanced by
either surface
chemistry &
In situ polymerisation
or mechanical
mixing in
solution/melt

After E.J. Kramer et al, Macromol **38 p8080 (1995)**

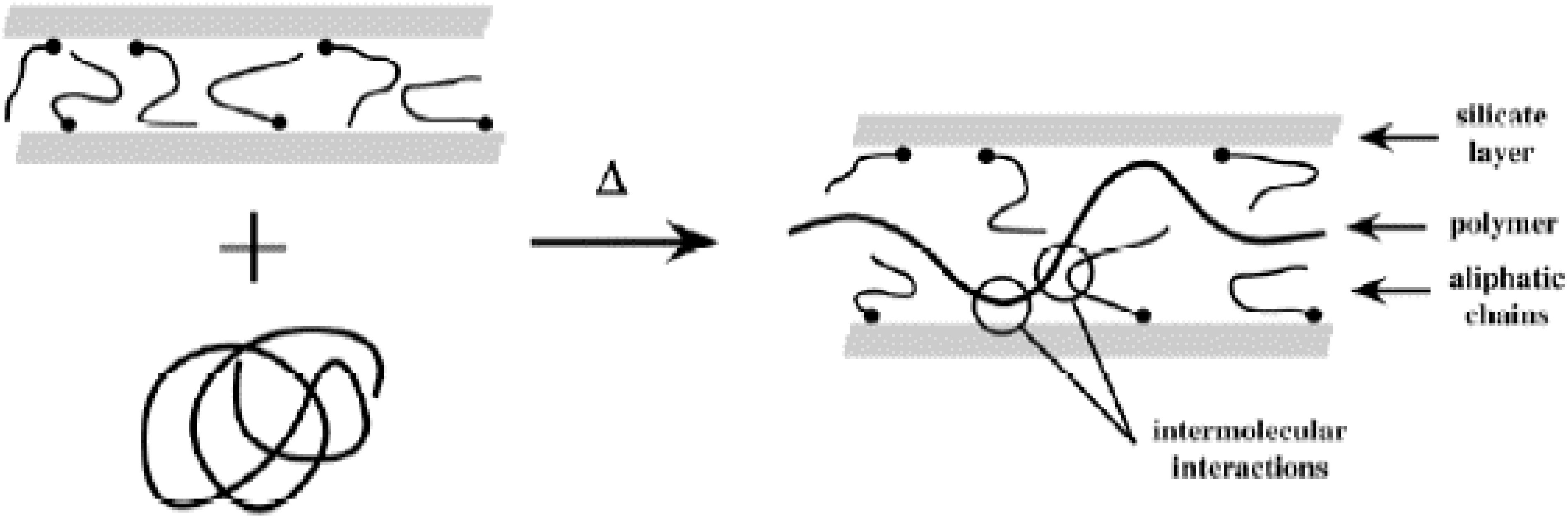
Ways of achieving Nanodispersion



Dispersion with chemistry (surfactants) or adequate mechanical work?

After E. Manias et al (various pubs)

Thermodynamics & Topology



Acts to

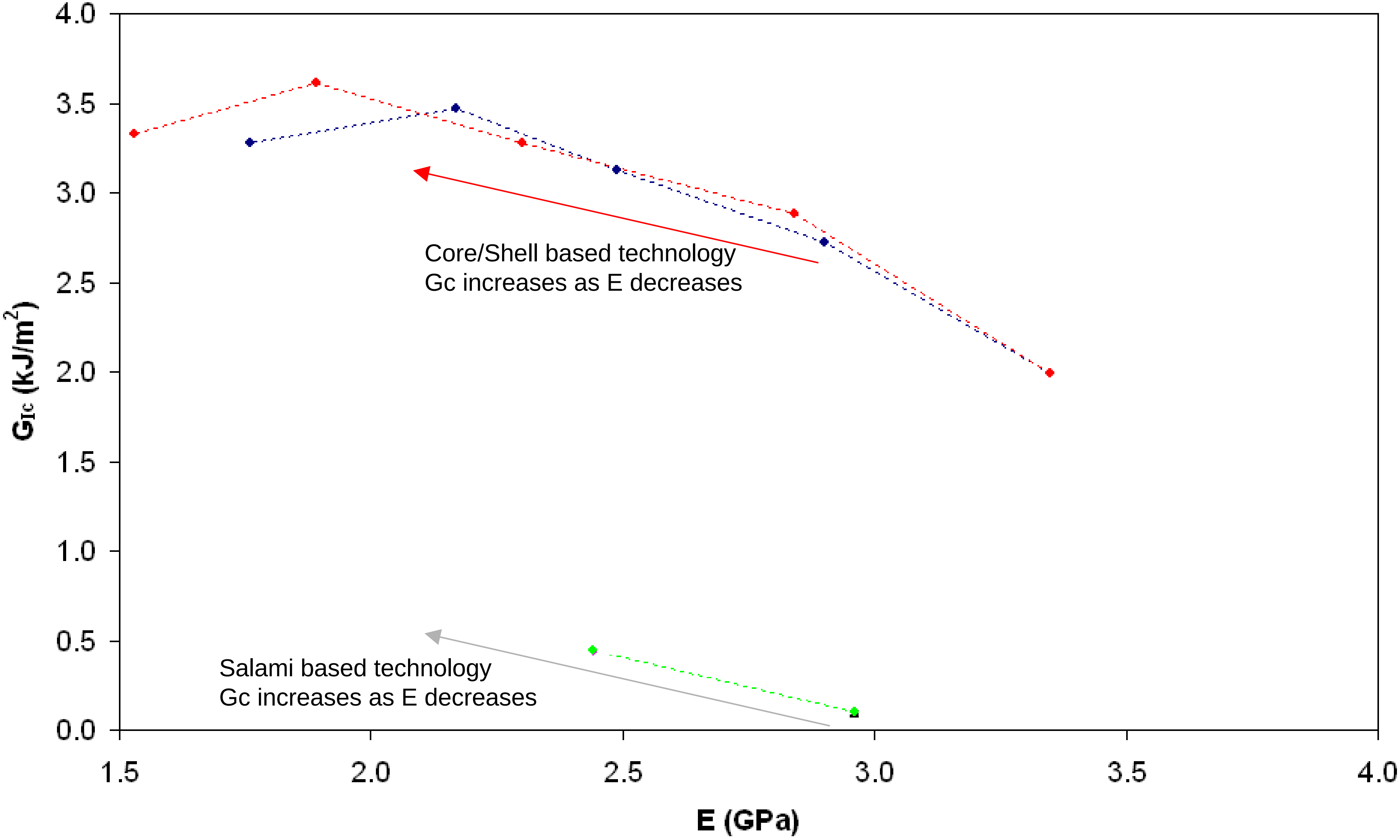
- Change free energy to allow mixing (entropic vs enthalpic balance)
    - Exfoliation (nanoscale) dispersion is target
- Topologically constrain polymer chains and suppress free volume

- Major property enhancements achieved if exfoliation reached

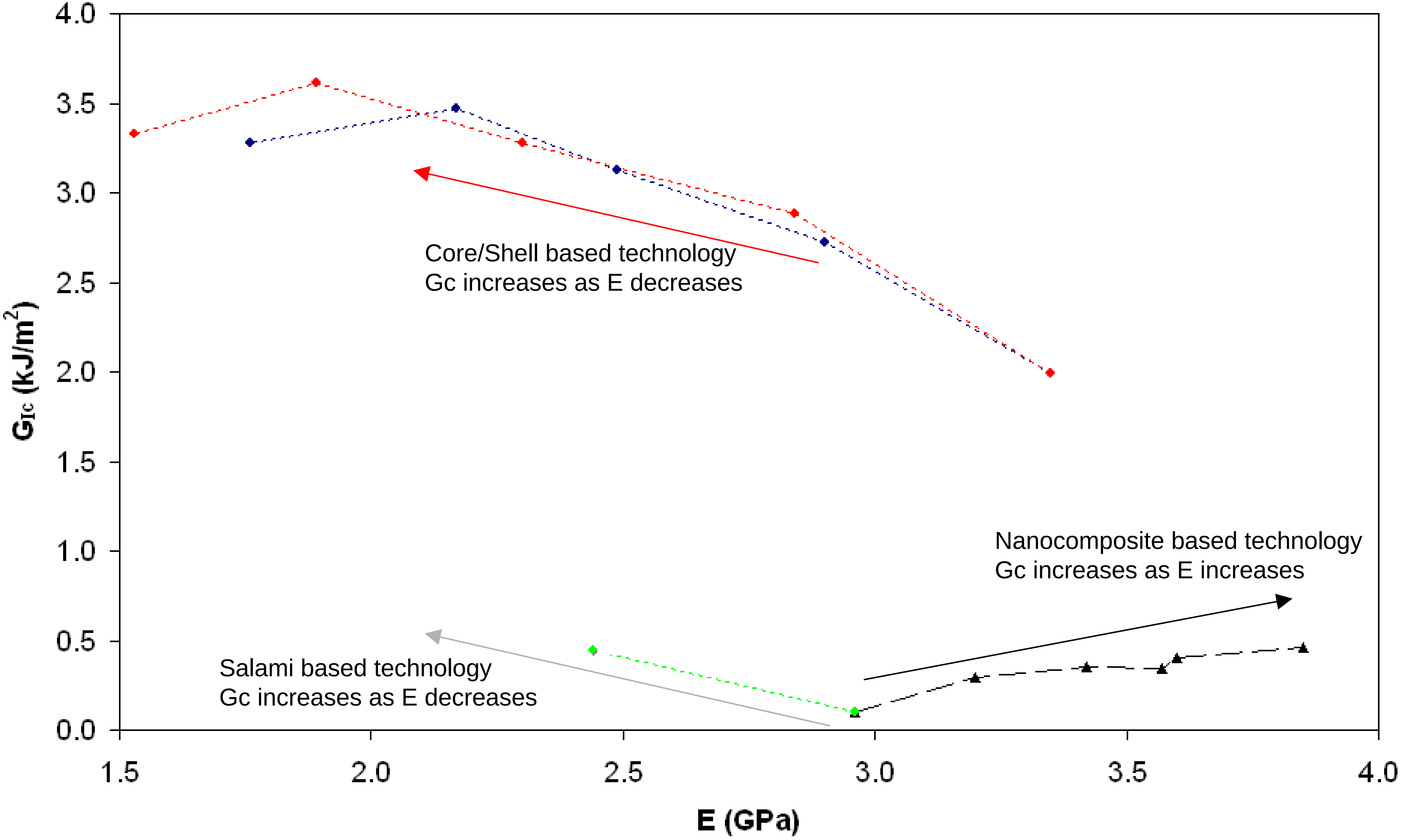
After E. Manias et al, Adv Poly Sci **138 p108 (1999)**

Exploitation

- Properties vs Performance
  - If cost of nanocomposites and cost of processing exceed the property increase, then commercially likely to fail
  - Nanocomposites are attractive because such small amounts (~5%) achieve major property shifts
  - Polymer nanocomposites are a different class of materials, with new science needed to predict their behaviour!



Salami results ex Kinloch et al (2005)



Nanosilicate results ex Kinloch et al (2005)

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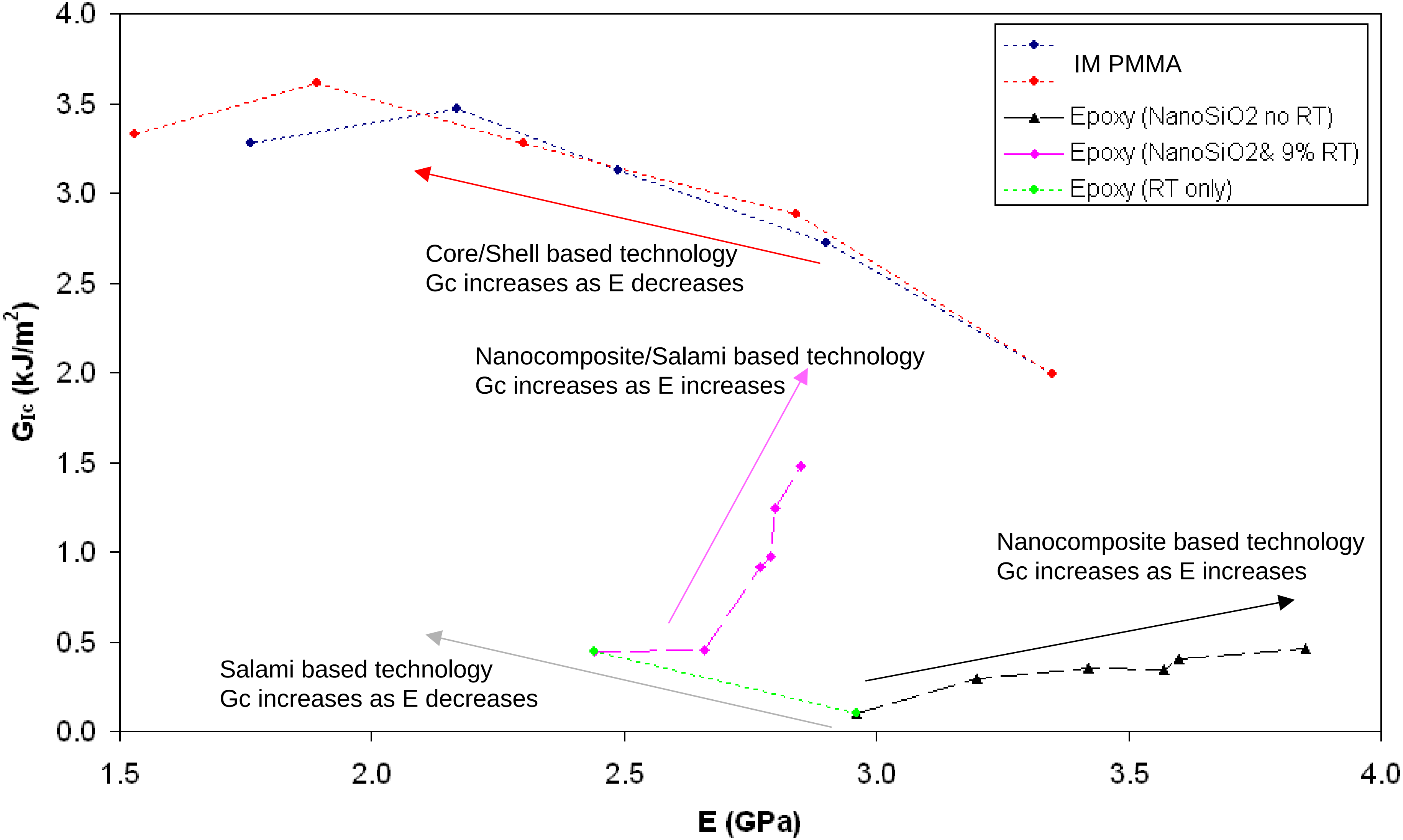
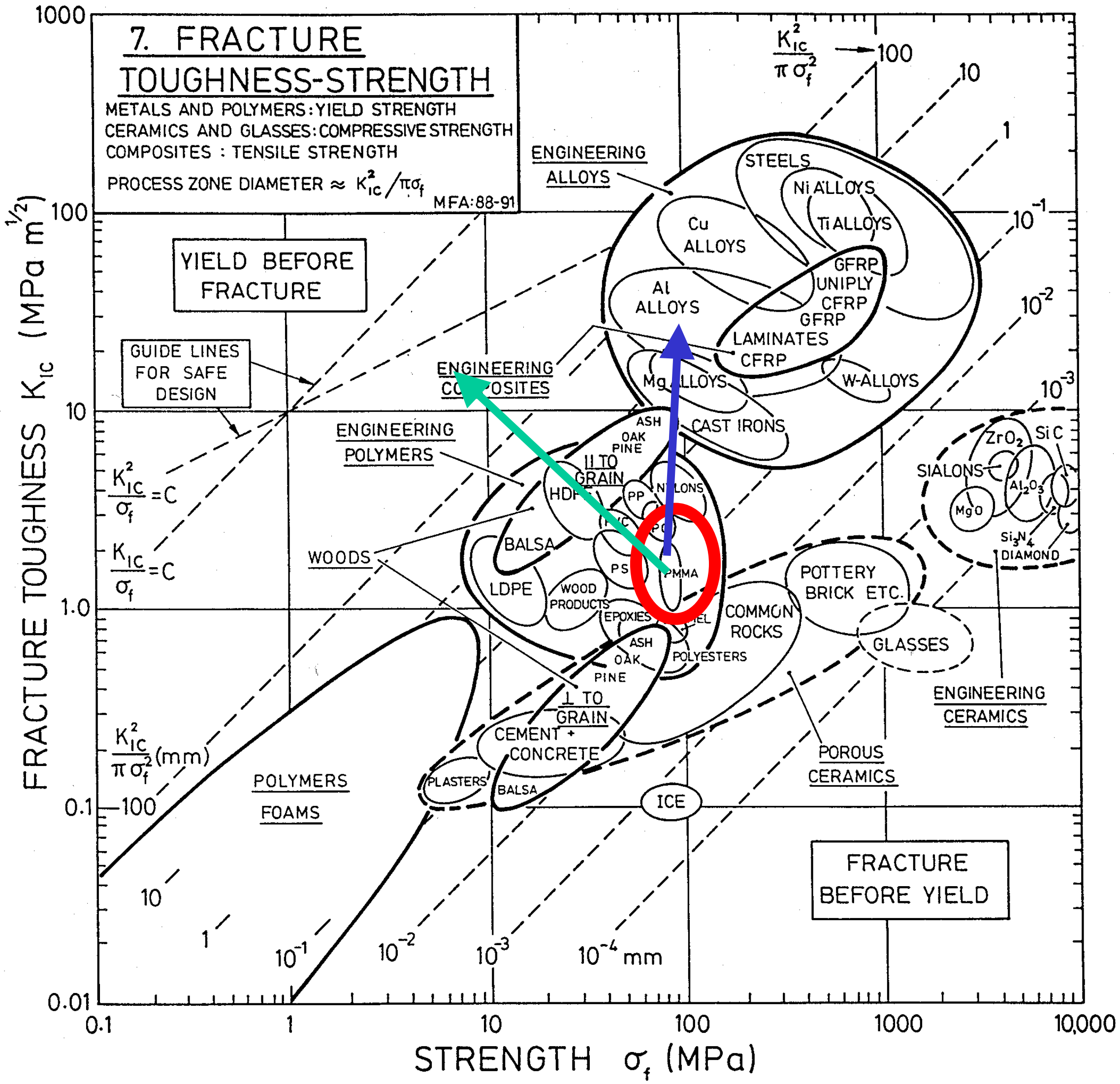


Salami, nanosilicate and mixed salami/ nanosilicate results ex Kinloch et al (2005)

Ashby - Materials Selection in Mechanical Design



PMMA

Materials Property ratio of importance

Rubber Technology

Nano & Rubber Technology

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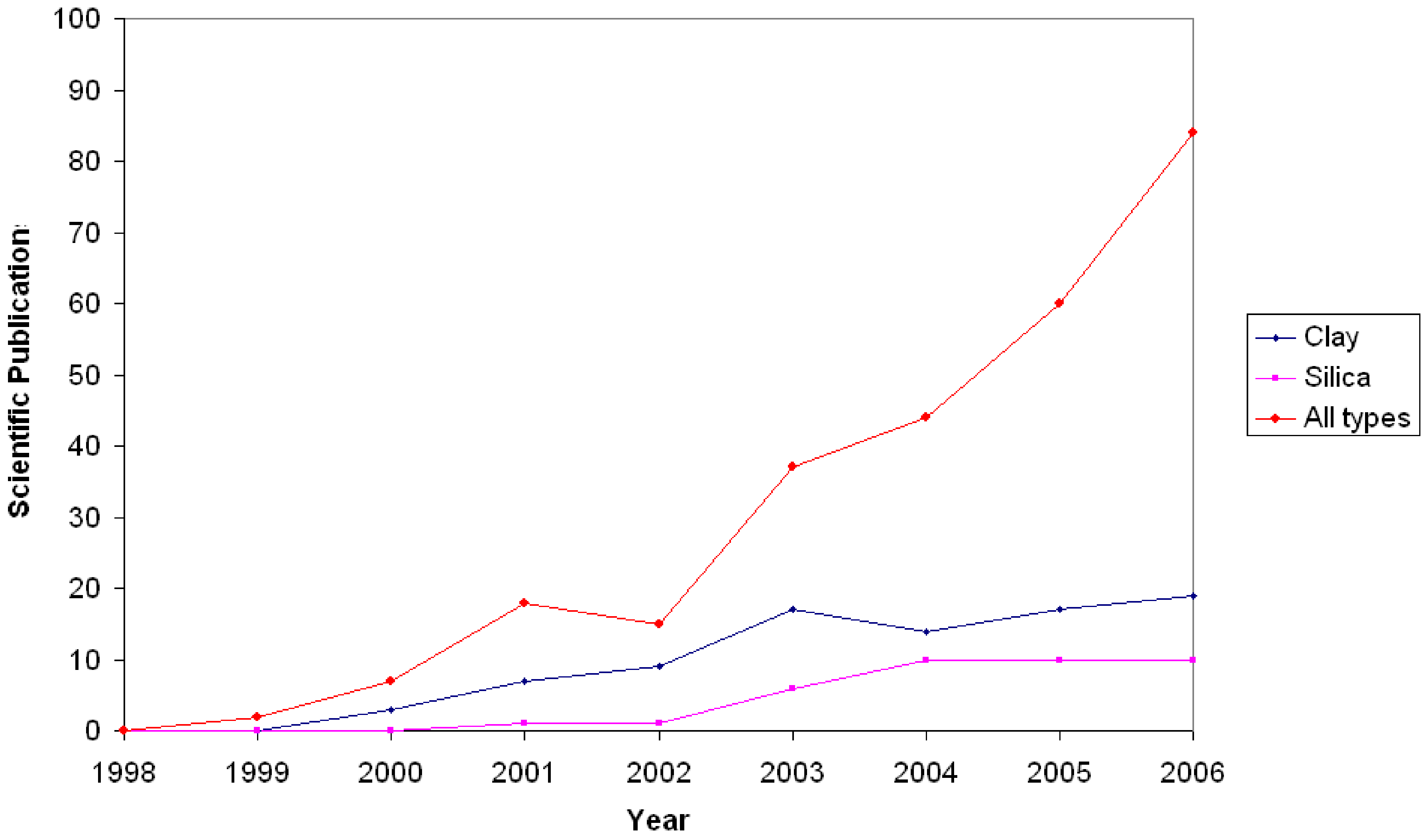
PMMA Nanocomposite Scientific Literature



‘Big Wish’ list measurement needs with Nanocomposites

- Mechanics
  - Long Term (Creep, Creep Rupture, Fatigue, ESC)
  - Short Term (Toughness)

- Dimensional Stability
  - (Permeation)

- Thermal Stability
  - (Esp Post Process)

- Fire
  - Cone Calorimetry

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Long Term Engineering Data
Life Assessment and Prediction

- Increasingly important due to global economy
  - Manufacturing base & end use is shifting to Far East
    - Ambient conditions are hotter/wetter/more sunlight cf Central European conditions where a lot of engineering data were generated

  - Can we develop both experimental and theoretical methods to cope with the changing patterns of use with **reliable** accelerated tests to cut both time and cost of data generation?

Life Assessment and Prediction

- Check methods outlined in
  'Practical guide to the assessment of the useful life of plastics'
  RP Brown RAPRA (2002)

- Examples Creep / Creep Rupture
  - Can they be applied under hotter/wetter conditions ?

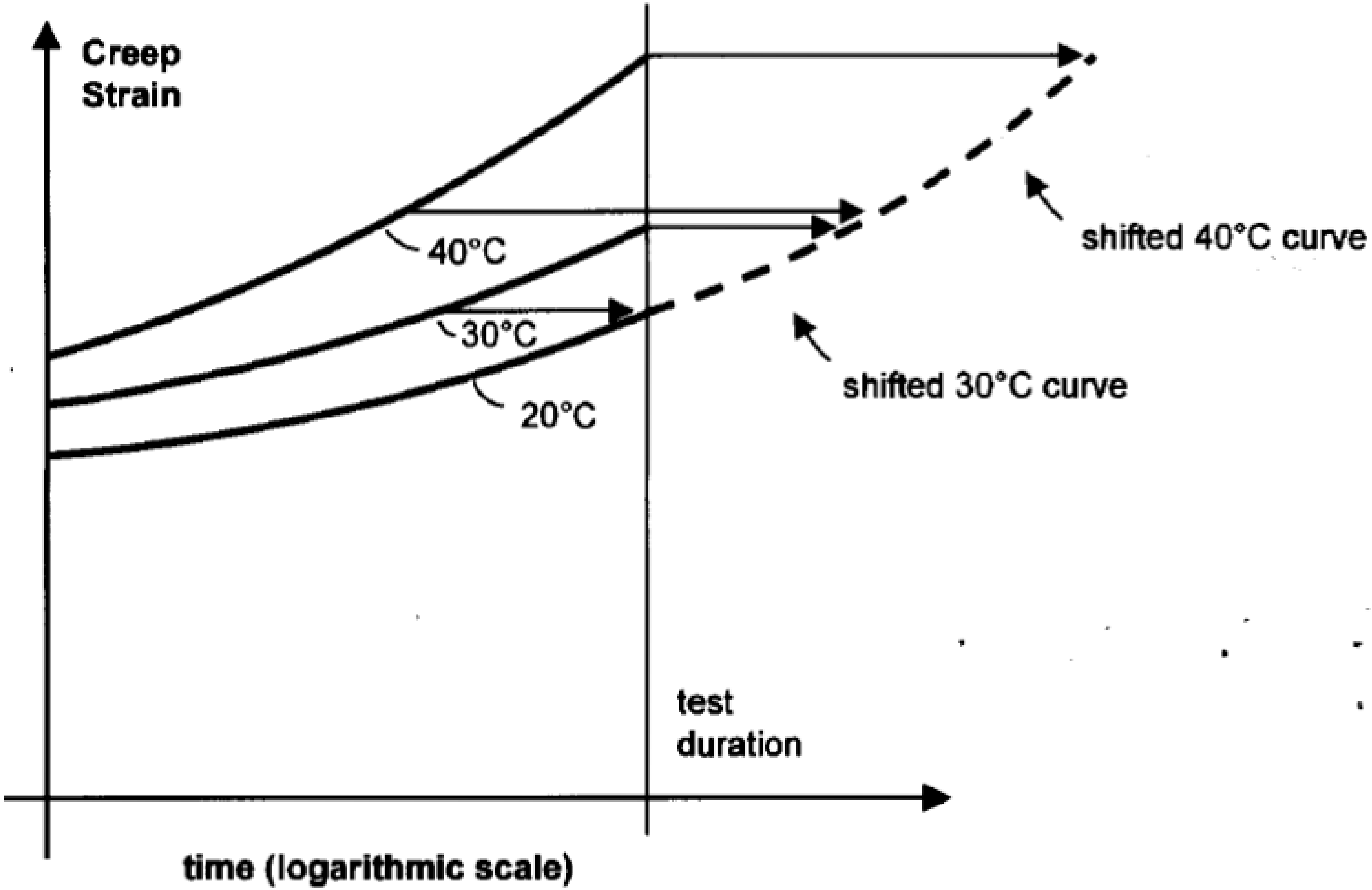

Figure 8.6 Simple time-temperature shifting of creep strain curves

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Life Assessment and Prediction

- Benefits would be reduced time/cost to generate desired data

  - BUT

- Not at expense of accuracy!

Life Assessment and Prediction

- Ultimate assurance is to keep long term stresses beneath critical value needed to initiate crazing
  - Crazing (Temp / Water / Solvents /etc)