Computational modelling for performance improvement of polymer nanocomposites

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http://www2.warwick.ac.uk/fac/sci/wmg/research/multifunctional_systems/lfigiel

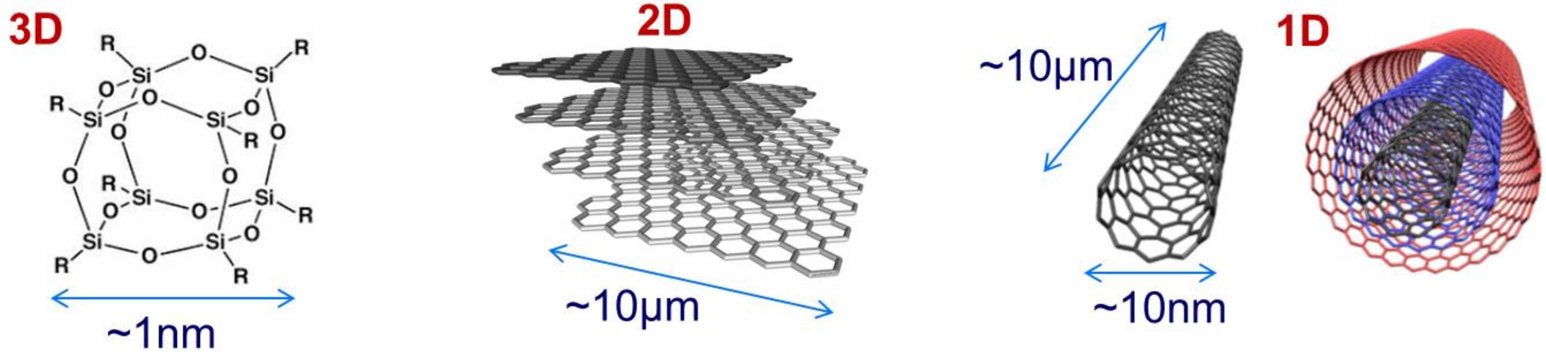
WMG Innovative Solutions

Warwick Centre for Predictive Modelling Seminar

28 May 2015

THE UNIVERSITY OF WARWICK

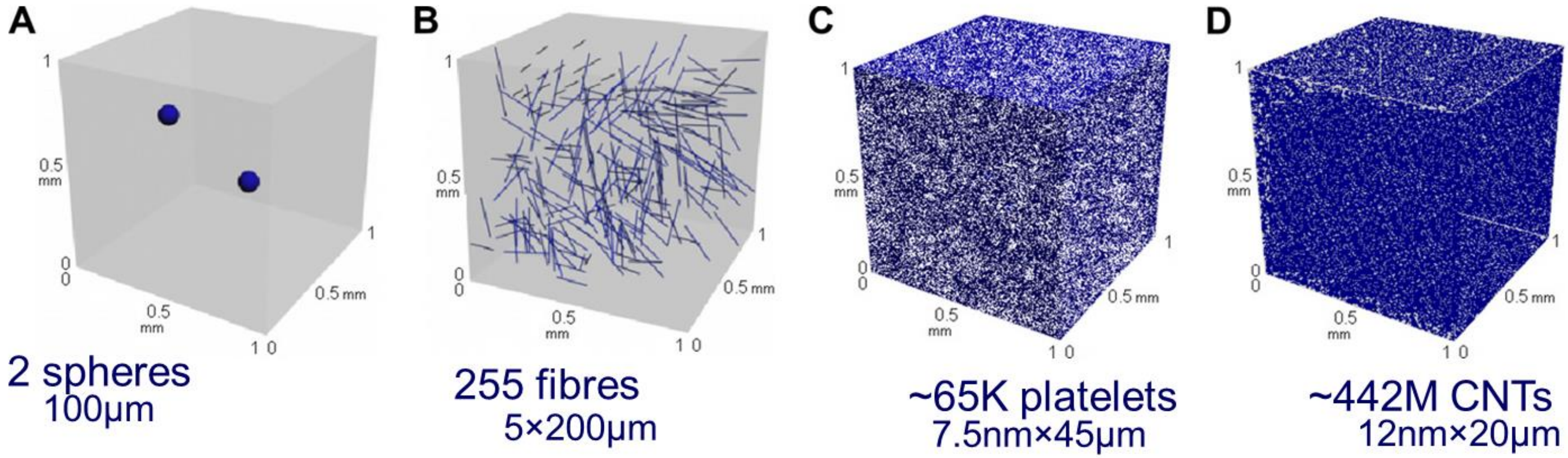
Polymer nanocomposites: polymers filled with nanoparticles at low loadings



Nanoparticle properties: *high stiffness; high conductivities, high surface-to-volume ratio*

Challenges: *dispersion/distribution and interfacial behaviour*

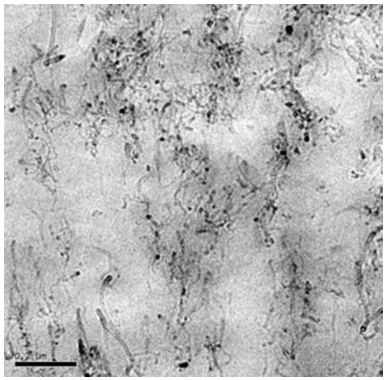
1mm^3 with 0.1% volume fraction



Ma et al. (2010), 41: 1345, Comp. Part A.

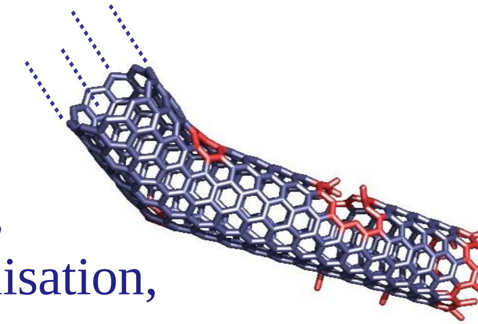
IINM Research

Understanding Materials at the Nanoscale & Linking with Macroscale

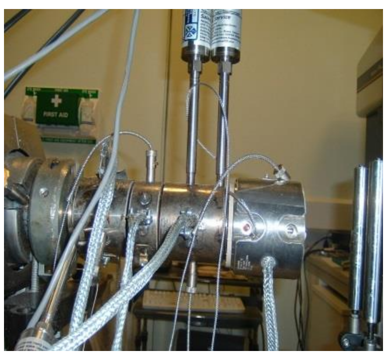


Dispersion & distribution; Polymer-nanoparticle interactions

Synthesis, functionalisation, defects

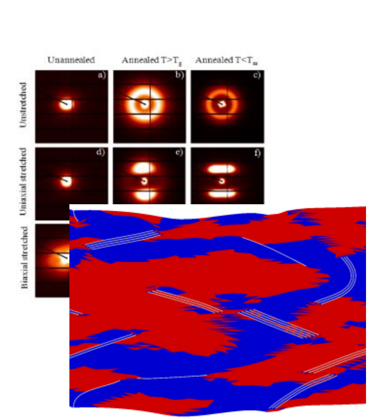


Controlled manufacturability at Scale



Tracking morphology in primary & secondary processing

In-situ characterisati & modelling



Delivering Material to the End User

IINM Team

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Polymer Science,
Processing,
Functional Materials

Dr Claire Dancer
Electromagnetic Materials,
Ceramics

Dr Vannessa Goodship
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Mechanics

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Characterisation,
Biomaterials

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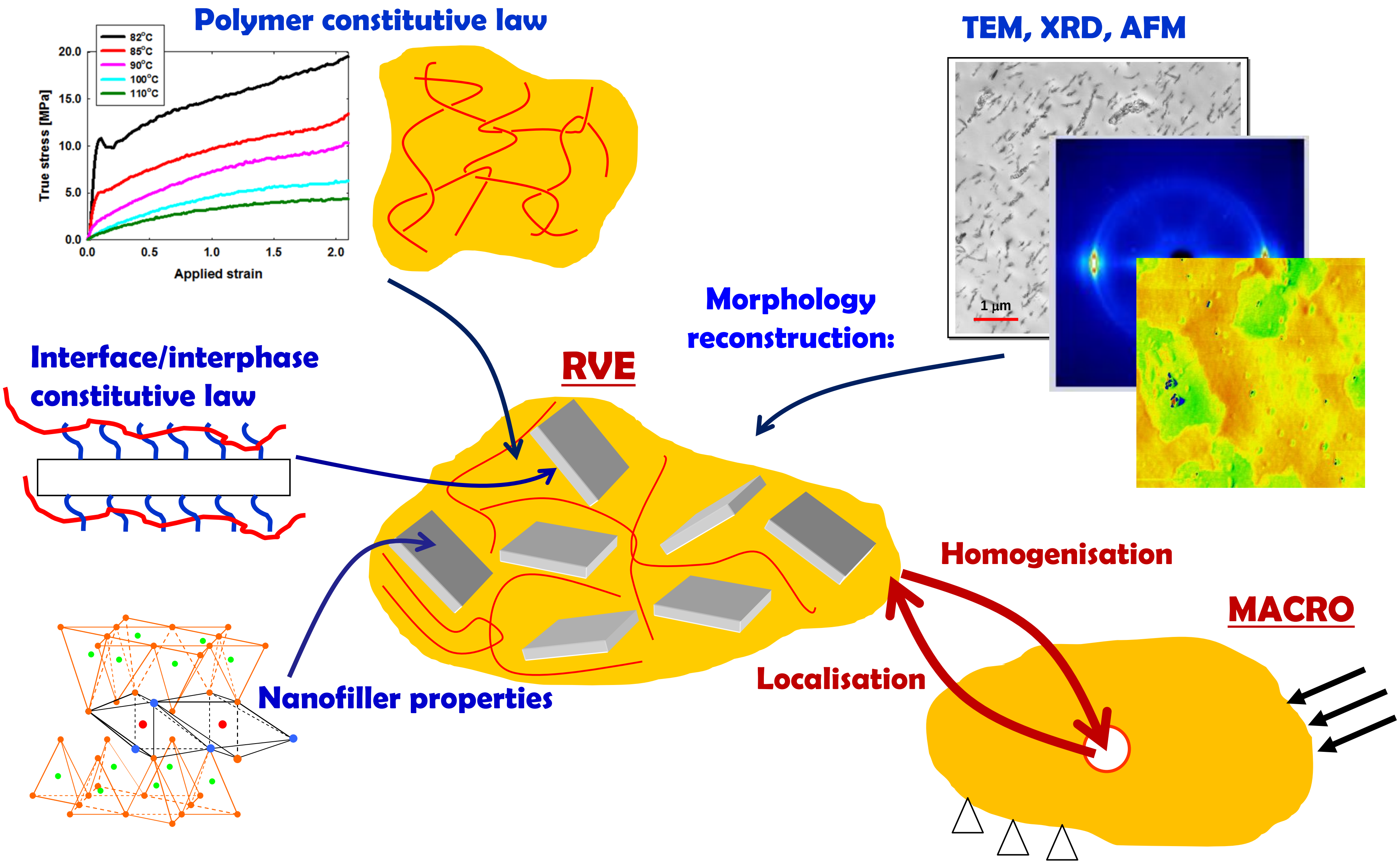
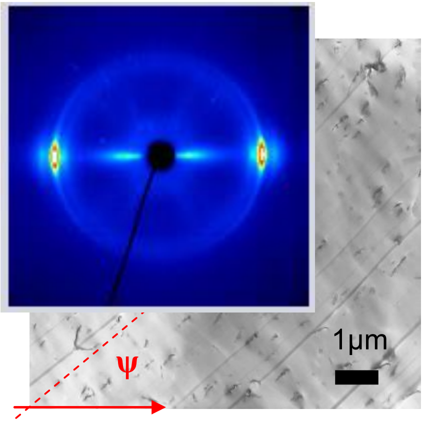
Modelling Methodology: overview

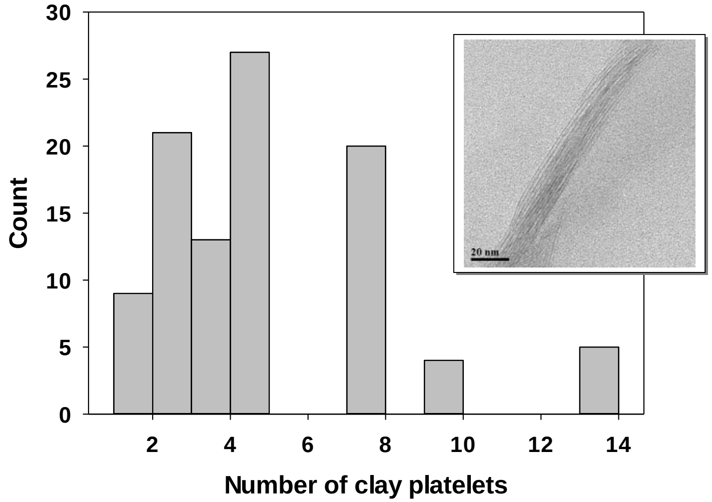


Reconstruction of initial morphology

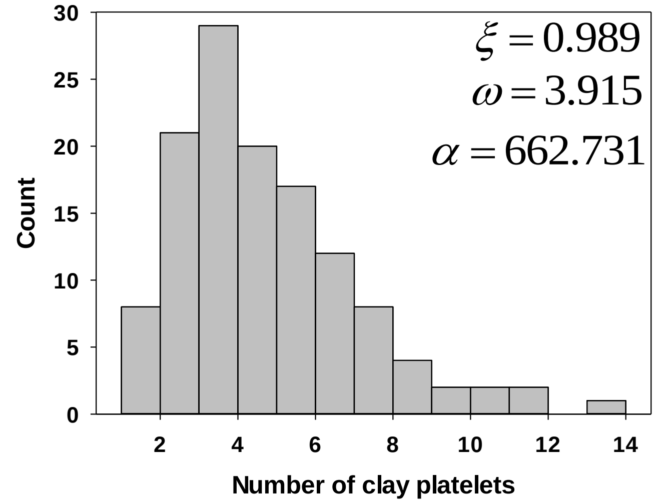
TEM/XRD



Experiment



Digital reconstruction

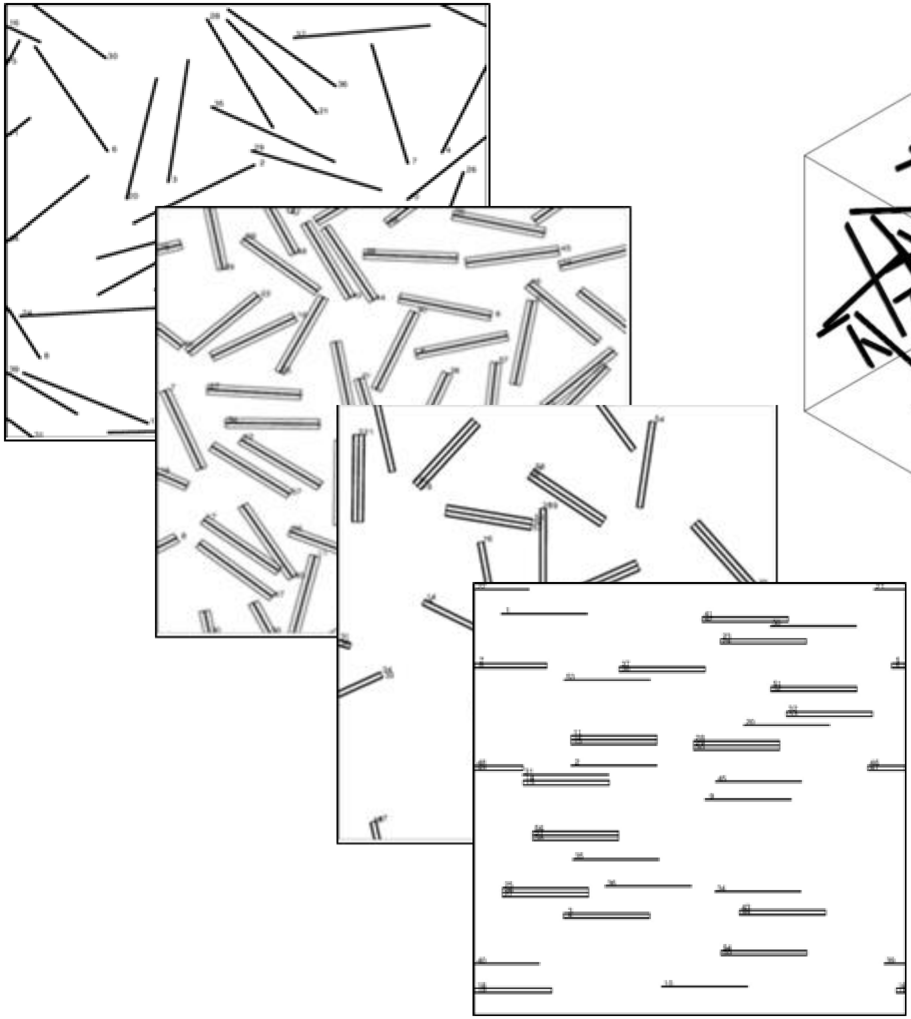


<u>Acceptance-rejection algorithm</u>

- Draw samples (e.g. orientation) from a given distribution (e.g. skew-Gaussian)
- Intersection/overlap checks
- Ensures global/local periodicity
- Implementation: Fortran (2D) and Python (3D)

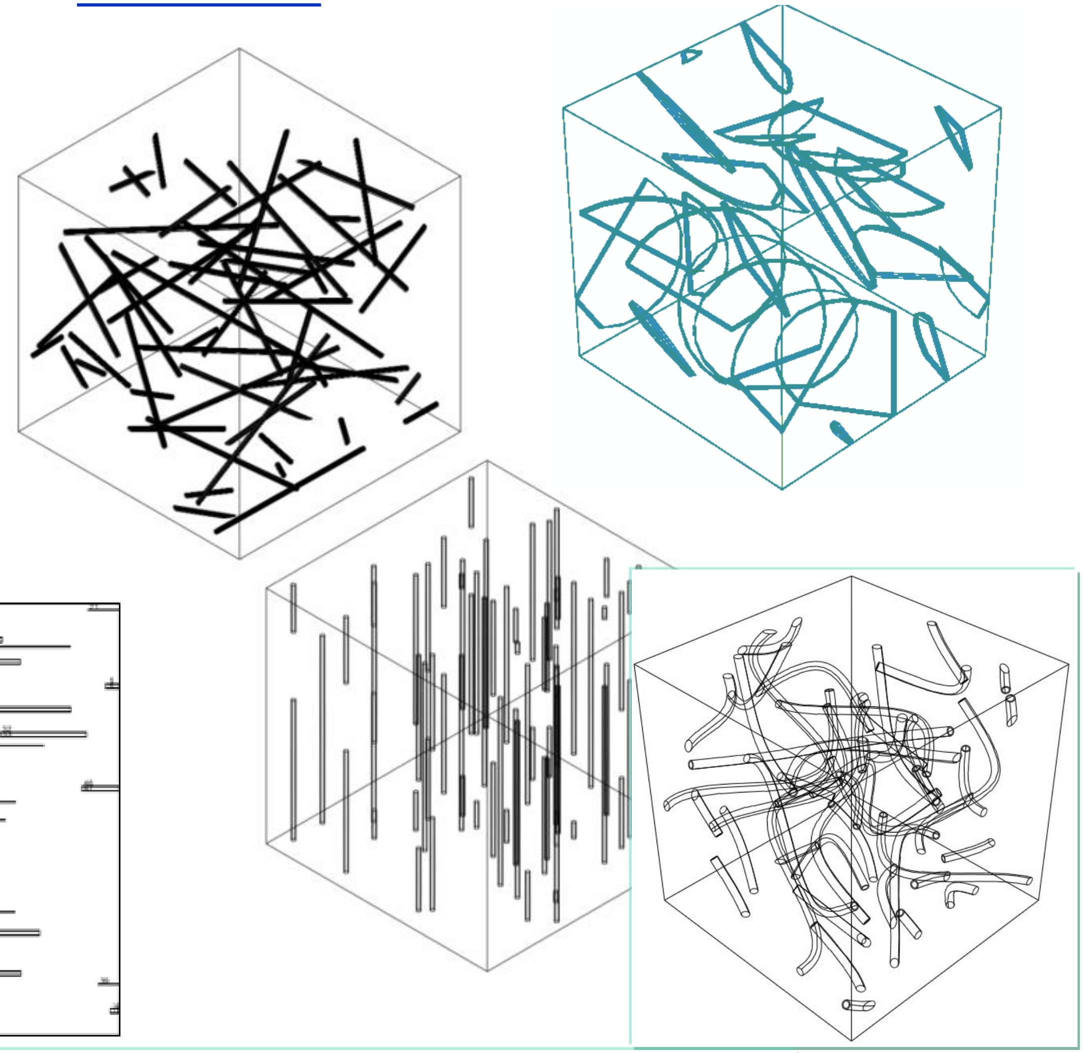
Examples of 2D and 3D models

2D models



Ł. Figiel/Computational Materials Science 84 (2014) 244–254

3D models

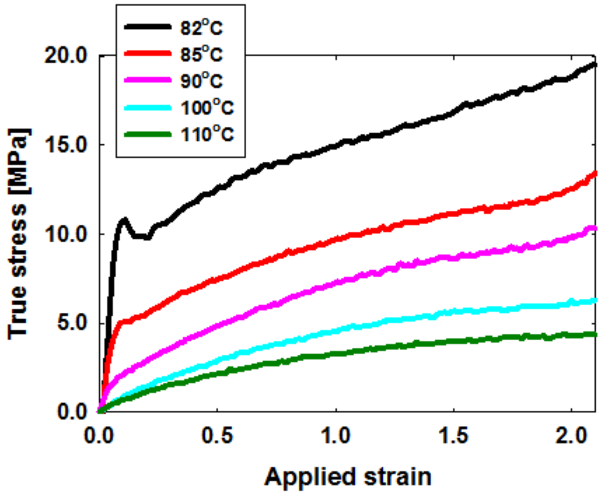


D. Weidt, Ł. Figiel/Computational Materials Science 82 (2014) 298–309

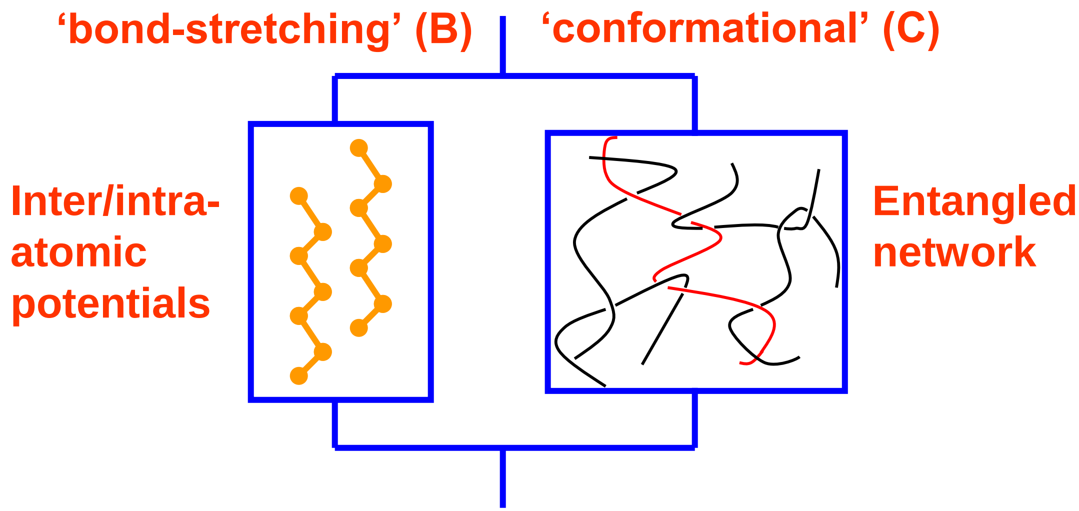
D. Weidt, Ł. Figiel/Composites Science and Technology 115 (2015) 52–59

Constitutive model: polymer matrix

Stress-strain behaviour around Tg - entangled polymer



Glass-rubber model



Total Cauchy stress tensor:

$$\boldsymbol{\sigma} = \hat{\boldsymbol{\sigma}}_B + \hat{\boldsymbol{\sigma}}_C + \sigma_m \boldsymbol{1} \quad \textit{where} \quad \sigma_m = K_B \ln J$$

Bond-stretching (B) stress tensor:

$$\overset{\circ}{\hat{\boldsymbol{\sigma}}}_B + \frac{\hat{\boldsymbol{\sigma}}_B}{\tau_B} = 2G_B \hat{\boldsymbol{D}} \quad \textit{where} \quad \tau_B = \tau_B\left(a_T, a_S, a_\sigma\right)$$

Conformational (C) stress tensor:

$$\hat{\sigma}_C^{(i)} = \frac{1}{J}\left(\hat{\lambda}_N^{(i)} \frac{\partial A_C}{\partial \hat{\lambda}_N^{(i)}} - \frac{1}{3}\sum_{k=1}^{3} \hat{\lambda}_N^{(k)} \frac{\partial A_C}{\partial \hat{\lambda}_N^{(k)}}\right) \quad \textit{where} \quad A_C = A_C\left(\hat{\lambda}_N^{(i)}, T, N_s, \alpha, \eta\right)$$

Stress-induced crystallisation:

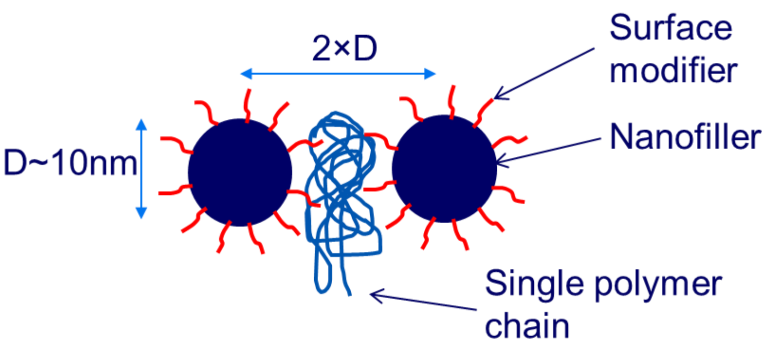
$$\hat{\sigma}_C \geq \hat{\sigma}_{C,crit} \quad \textit{where} \quad \hat{\sigma}_{C,crit} = \hat{\sigma}_{C,crit}\left(a_T, a_{s(S)}, \hat{\boldsymbol{D}}\right)$$

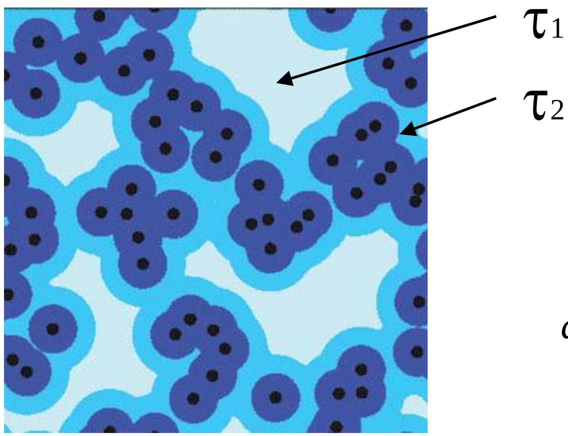
C.P. Buckley, C.Y. Lew / Polymer 52 (2011) 1803–1810

Ł. Figiel *et al* Modelling Simul. Mater. Sci. Eng. **18** (2010) 015001

L. Figiel, C.P. Buckley / International Journal of Non-Linear Mechanics 44 (2009) 389–395

Constitutive model: interface/interphase/gallery





Qiao et al. (2011), 49:740, J. Pol. Phys. B

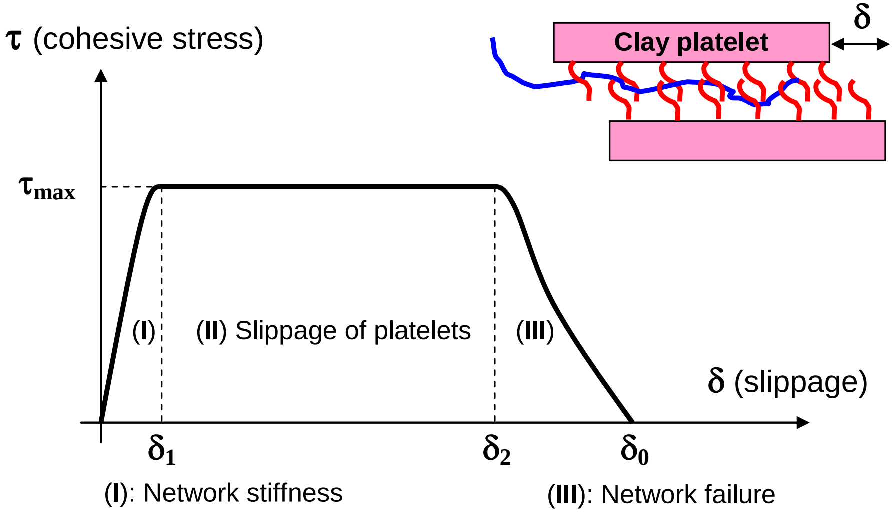
$$\tau_i = \tau_{ref} a_T a_S a_\sigma$$

$$a_T = \exp\left[\left(\frac{\Delta H}{R}\right)\left(\frac{1}{T} - \frac{1}{T_{ref}^{INT}}\right)\right]$$

$$a_S = \exp\left[\frac{C_V}{T_f - T_\infty} - \frac{C_V}{T_{ref}^{INT} - T_\infty}\right]$$

$$\tan\delta_M(\omega_t, \mathrm{T}_{ref}^{INT}) = \frac{E_M^{''}(\omega_t, \mathrm{T}_{ref}^{INT})}{E_M^{'}(\omega_t, \mathrm{T}_{ref}^{INT})}$$

Ł. Figiel / Computational Materials Science 84 (2014) 244–254



C. Pisano, Ł. Figiel / Composites Science and Technology 75 (2013) 35–41

$$\tau = \tau_{\max} f(\delta)$$

(I) $f(\delta) = 2\frac{\delta}{\delta_1} - \left(\frac{\delta}{\delta_1}\right)^2$ if $\delta < \delta_1$;

(II) $f(\delta) = 1$ if $\delta_1 < \delta < \delta_2$

(III) $f(\delta) = 2\left(\frac{\delta - \delta_2}{\delta_0 - \delta_2}\right)^3 - 3\left(\frac{\delta - \delta_2}{\delta_0 - \delta_2}\right)^2 + 1$ if $\delta_1 < \delta < \delta_2$,

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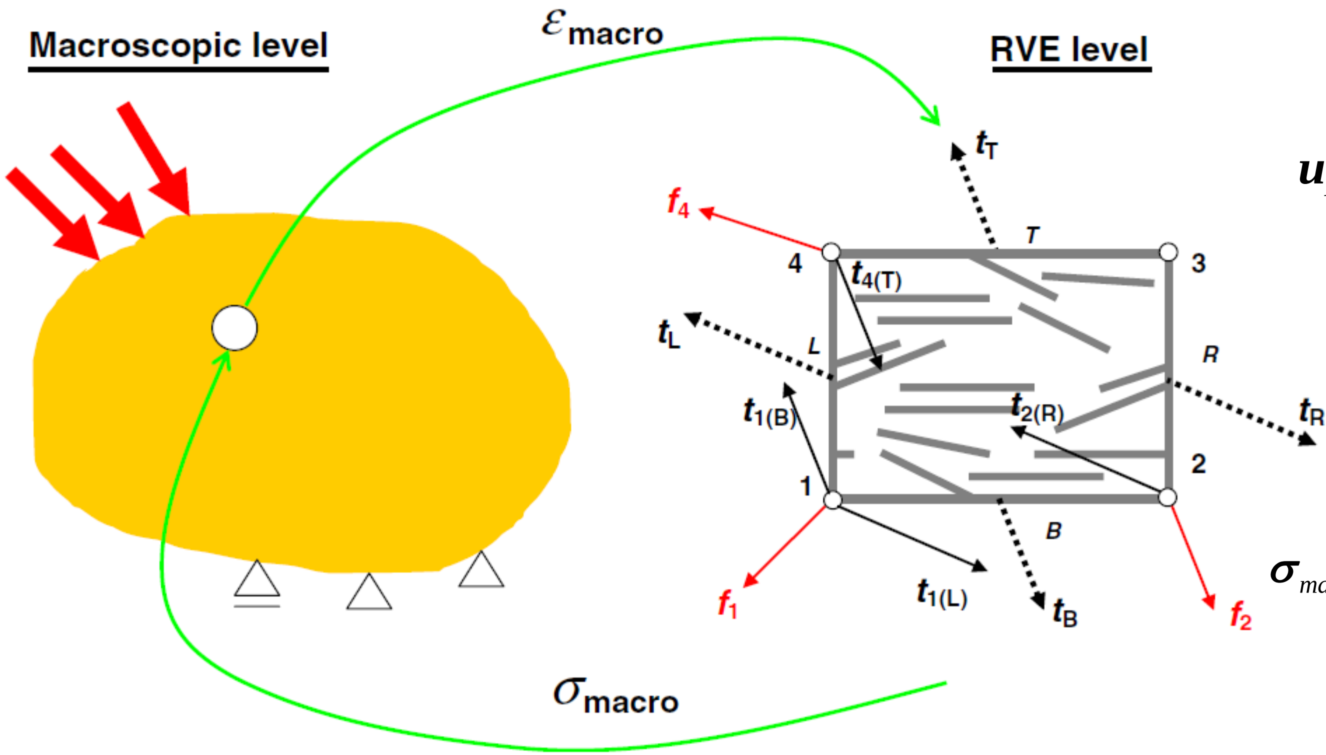
Scale transitions: macro-to-RVE & RVE-to-macro



Mechanical field

$$\boldsymbol{u}_{RVE}\left(\boldsymbol{x}\right)=\boldsymbol{\varepsilon}_{\mathrm{macro}}\boldsymbol{X}\;+\boldsymbol{u}_{f}\left(\boldsymbol{x}\right)$$

$$\boldsymbol{\varepsilon}_{\mathrm{macro}}=\boldsymbol{F}_{\mathrm{macro}}-\boldsymbol{1}$$

$$\boldsymbol{\sigma}_{macro}=\frac{1}{V_{\mathrm{RVE}}}\int_{V_{\mathrm{RVE}}}\boldsymbol{\sigma}_{\mathrm{RVE}}\left(\boldsymbol{x}\right)\,dV_{\mathrm{RVE}}$$

$$=\frac{1}{V_{\mathrm{RVE}}}\int_{\Gamma_{\mathrm{RVE}}}\boldsymbol{t}\otimes\boldsymbol{x}\;d\Gamma_{\mathrm{RVE}}$$

$$=\frac{1}{V_{\mathrm{RVE}}}\sum_{I=1}^{N}\boldsymbol{f}_{(I)}\otimes\boldsymbol{x}_{(I)}$$

Non-mechanical field

$$\theta_{RVE}\left(\boldsymbol{x}\right)=\theta_{RVE}^{ref}+\nabla_{\mathrm{macro}}\theta_{macro}\cdot\boldsymbol{x}+\theta_{f}\left(\boldsymbol{x}\right)$$

$$q_{RVE}=\frac{1}{V_{\mathrm{RVE}}}\int_{V_{\mathrm{RVE}}}q_{\mathrm{RVE}}\left(\boldsymbol{x}\right)\,dV_{\mathrm{RVE}}$$

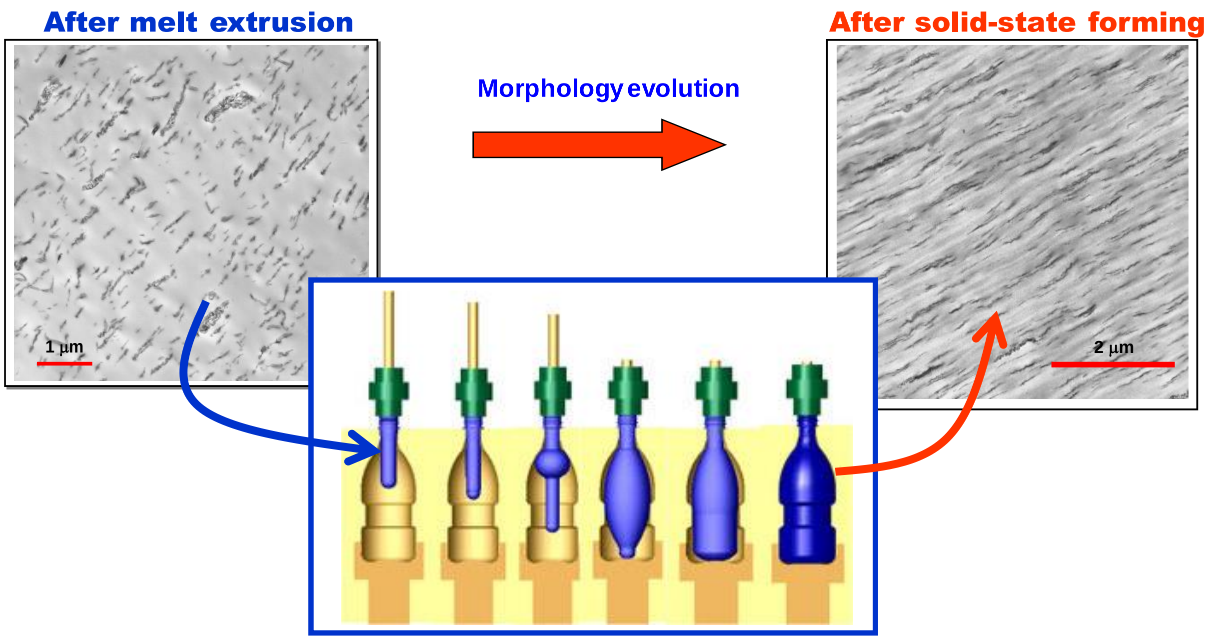
Tangent operator

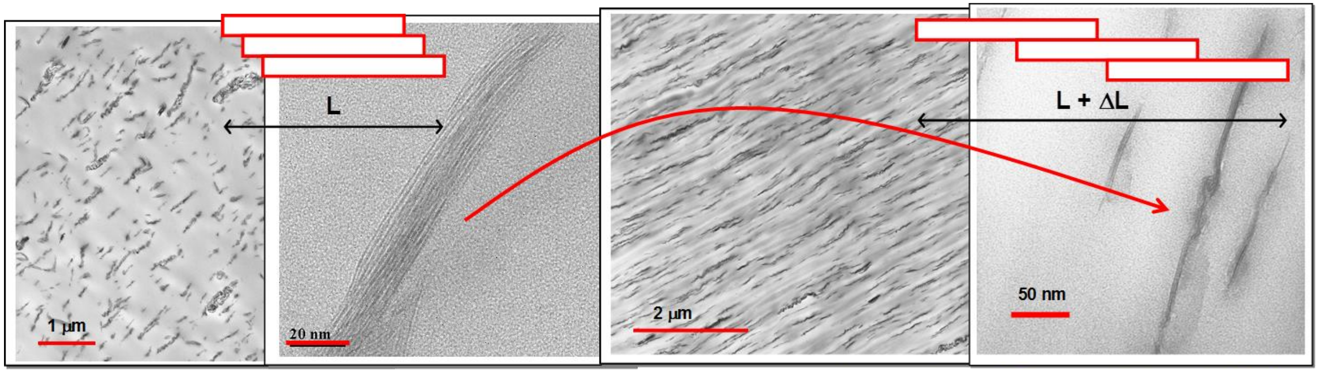
$$\boldsymbol{C}_{macro}=\frac{\partial\boldsymbol{\sigma}_{macro}}{\partial\boldsymbol{\varepsilon}_{macro}}$$

I. Özdemir et al. / Comput. Methods Appl. Mech. Engrg. 198 (2008) 602–613

Ł Figiel *et al* Modelling Simul. Mater. Sci. Eng. **18** (2010) 015001

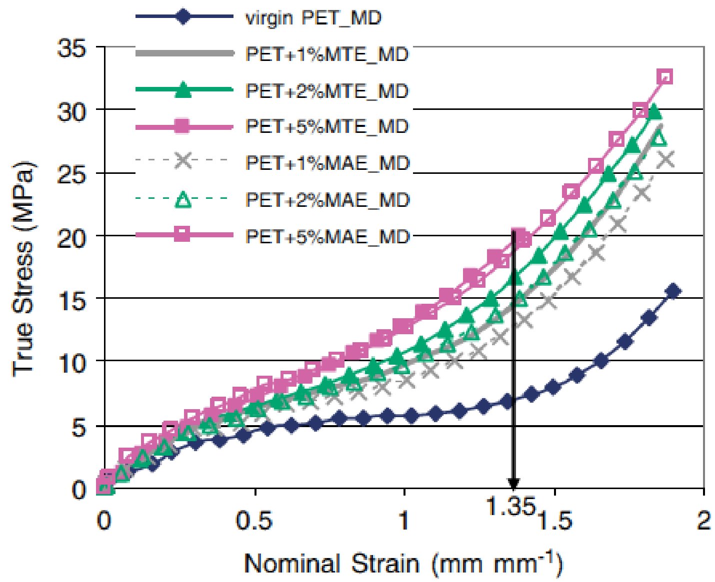
Case study 1: Secondary processing near Tg



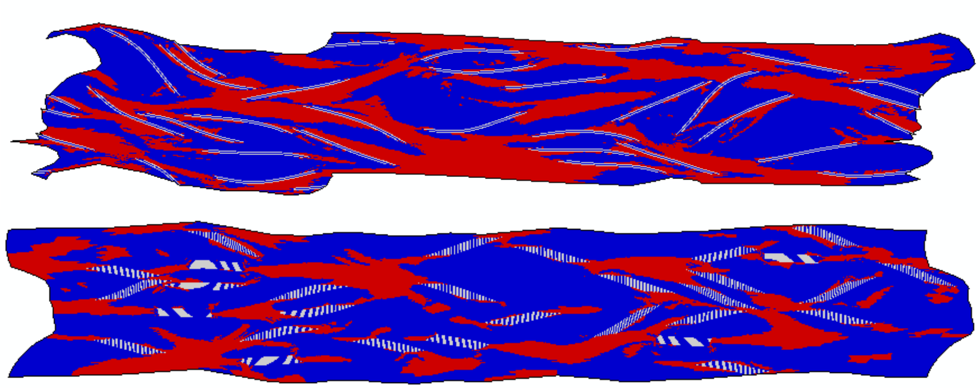


by courtesy of Queens University Belfast

Experiment



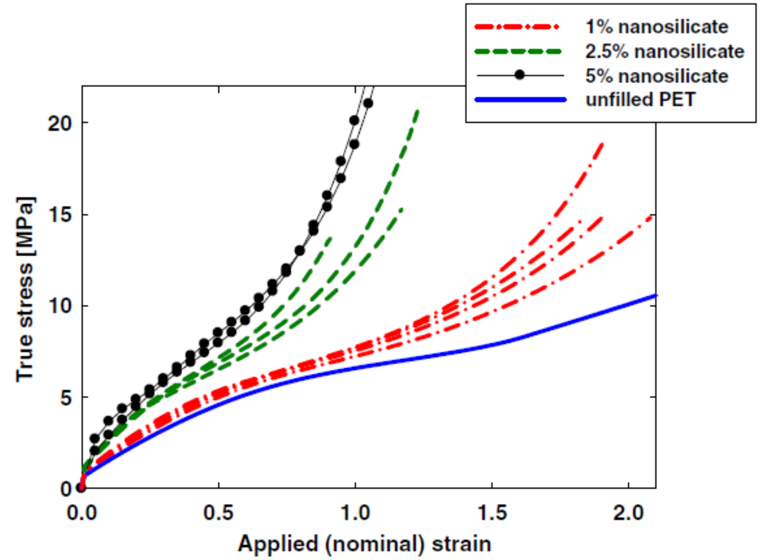
KH Soon *et al.* *Polym Int* 2009; **58**: 1134–1141

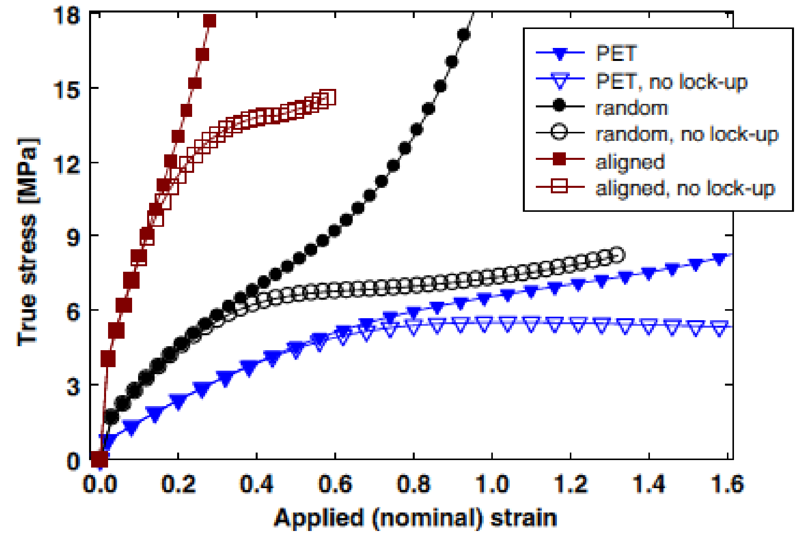


Viscous flow

Stress-induced crystallisation

Simulation



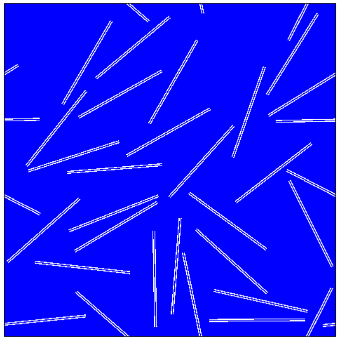


Ł Figiel *et al* Modelling Simul. Mater. Sci. Eng. **18** (2010) 015001

Morphology evolution with applied deformation

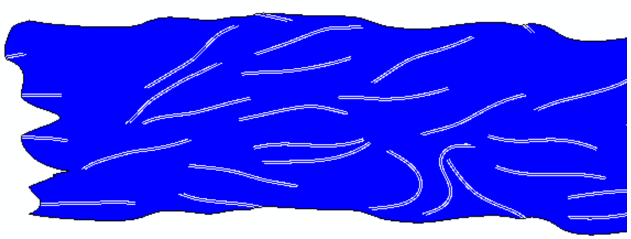
TEM image analysis

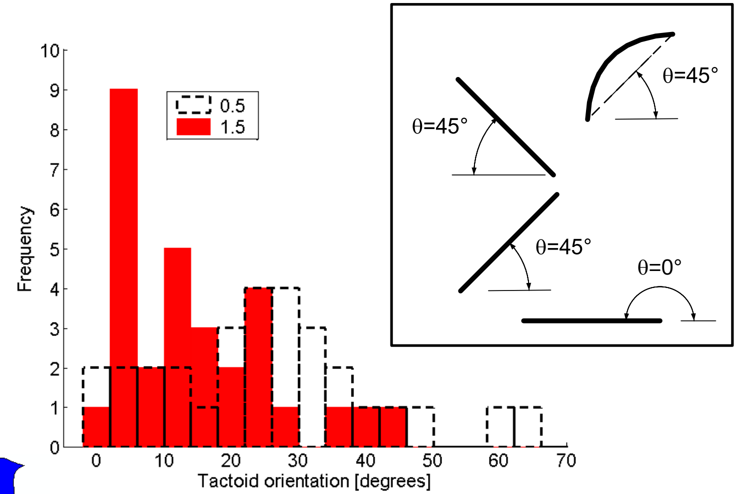
Unstretched

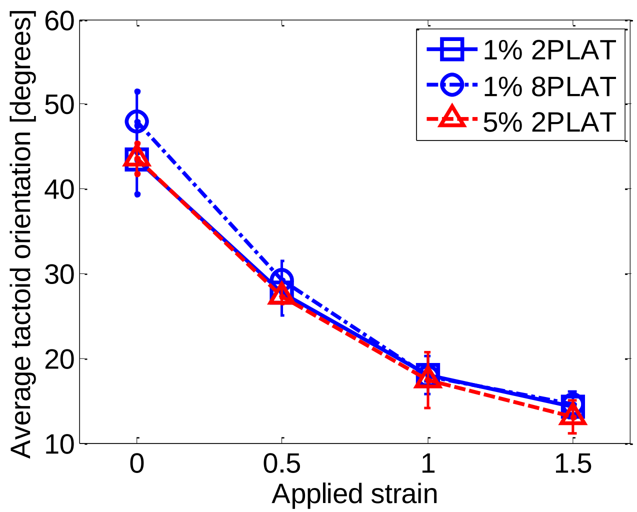


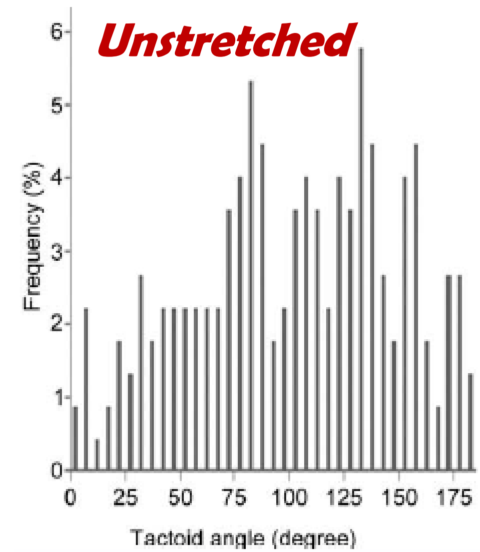
(Applied) Strain ~1

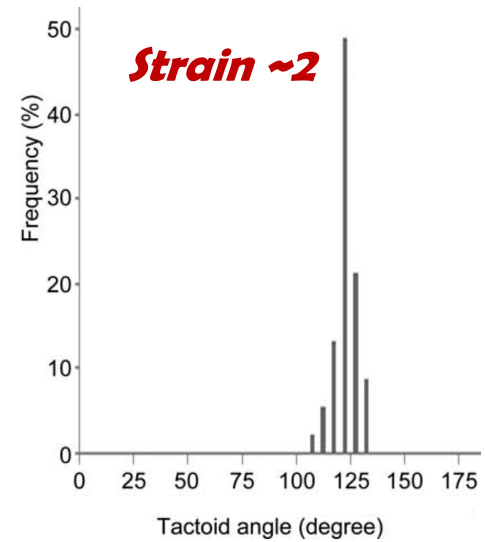
Strain ~1.5







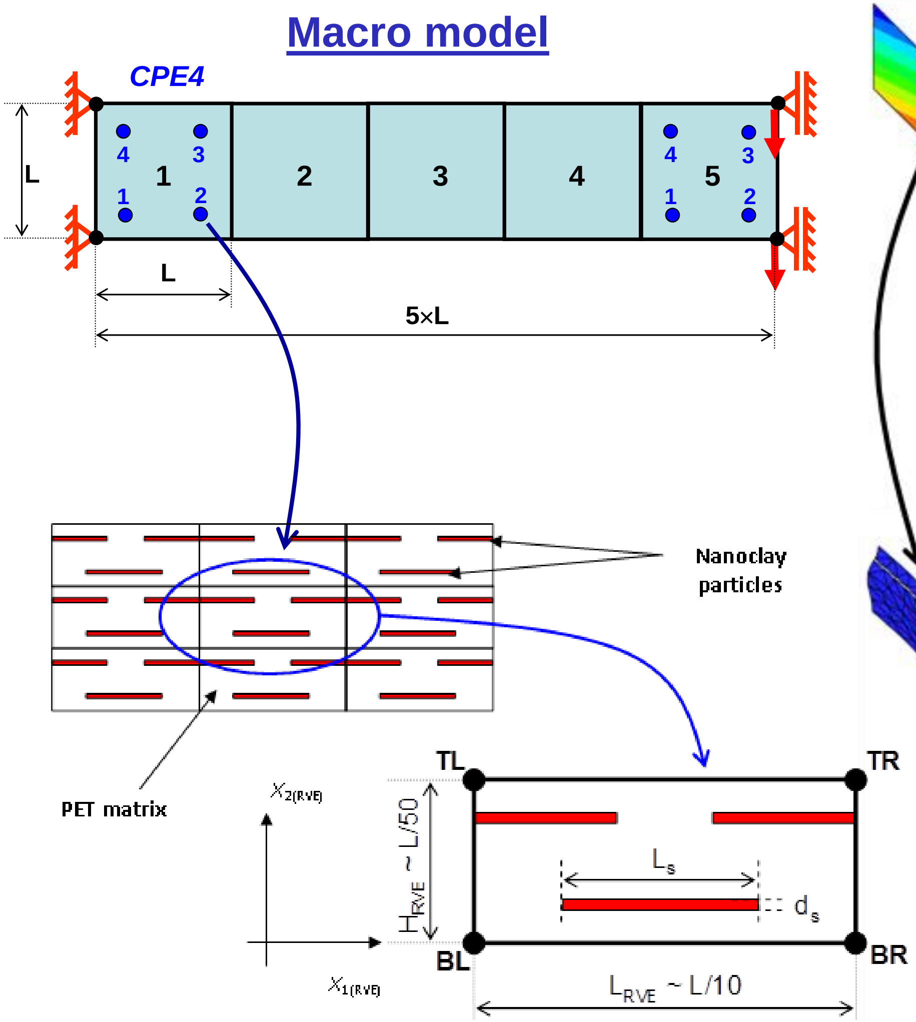


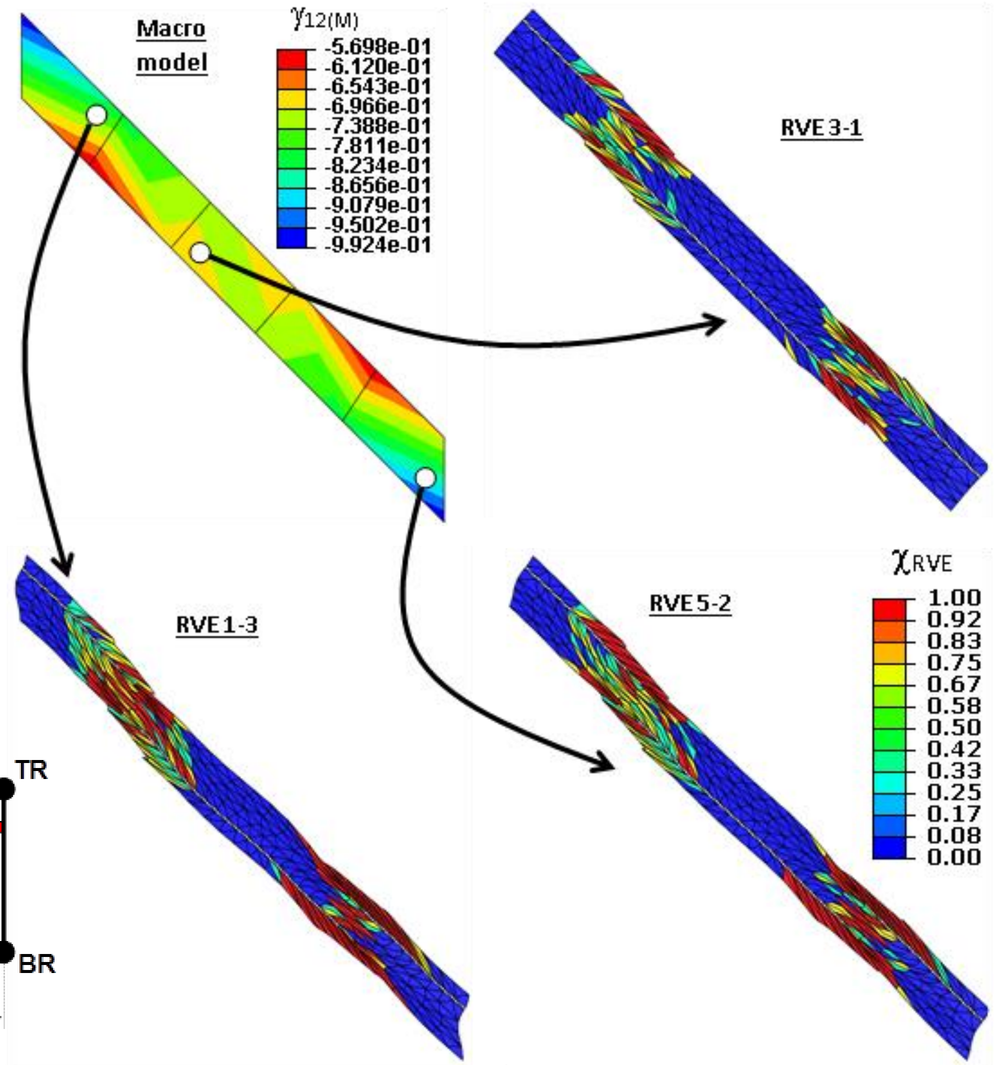


C. Pisano, Ł. Figiel / Composites Science and Technology 75 (2013) 35–41

KH Soon *et al.* *Polym Int* 2009; **58**: 1134–1141

Nanocomposite sheet during thermoforming (100^0C, $1s^{-1}$)





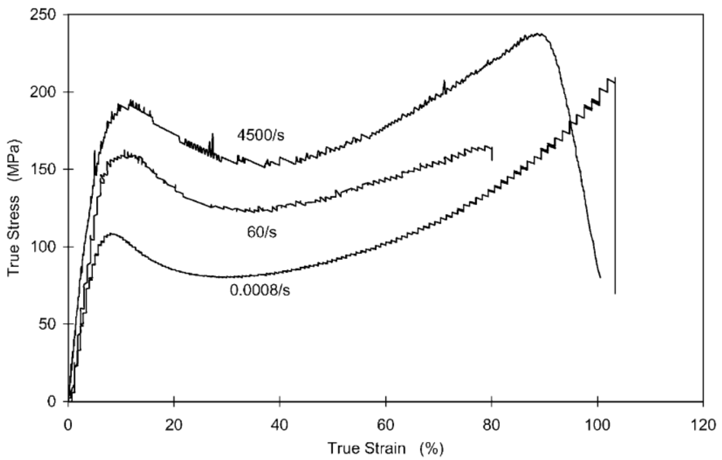
AIP Conf. Proc. 1353, 1226-1231 (2011); doi: 10.1063/1.3589684

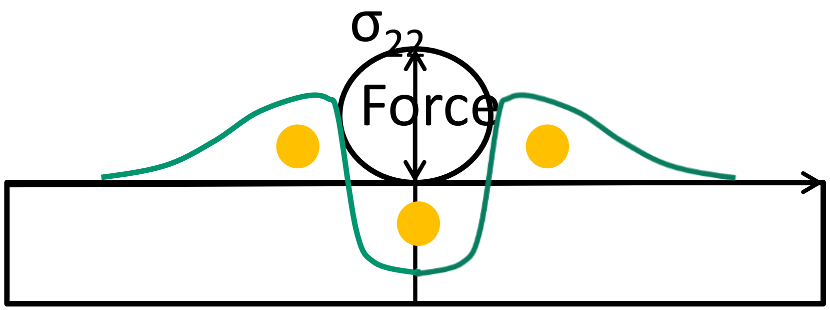
Case study 2: Rate-dependent response

- **CFRP laminates under impact loading**
  Opening of matrix cracks (brittle nature of epoxy)
  → delamination at the interfaces, structural degradation

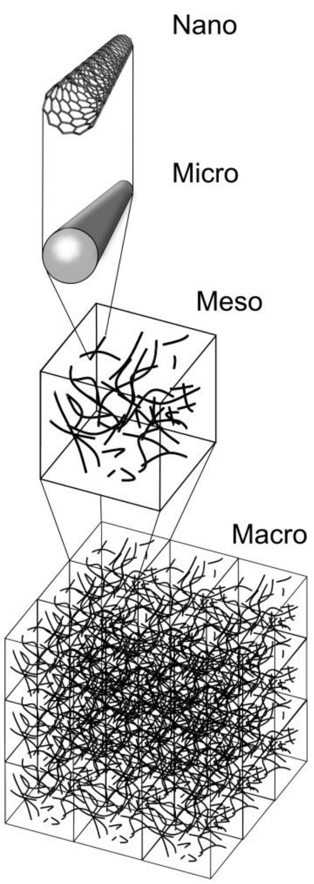
- **Hypothesis:** **CNT/epoxy surface coating will enhance the impact resistance** due to an increase in energy dissipation/absorption.

(1) an enhanced nonlinear deformation of the matrix
(2) CNT pullout in form of CNT crack bridging





MWCNT properties



Elastic constants

$$E_{33}^{\text{zig-zag}} = \frac{4\sqrt{3}\mathrm{C}_r}{\left(r_{\mathrm{CNT}}/2\right)\left[9+3\left(\mathrm{C}_r r_0^2/\mathrm{C}_\theta\right)/\left(2\eta_2\right)\right]}$$

$$\nu_{31}^{\text{zig-zag}} = \frac{-1+\left(\mathrm{C}_r r_0^{\,2}/\mathrm{C}_\theta\right)/\left(2\eta_2\right)}{3+\left(\mathrm{C}_r r_0^{\,2}/\mathrm{C}_\theta\right)/\left(2\eta_2\right)}$$

$$G_{31}^{\text{zig-zag}} = \frac{8\sqrt{3}n^2 sin^2\left(\pi/2n\right)\mathrm{C}_r}{\left(r_{\mathrm{CNT}}/2\right)\pi^2\left(6+\mathrm{C}_r r_0^{\,2}/\mathrm{C}_\theta\right)}$$

$$\eta_2 = \frac{14+12cos\left(\pi/n\right)-2cos^2\left(\pi/n\right)}{10+4cos\left(\pi/n\right)-6cos^2\left(\pi/n\right)}$$

Shen and Li (2004) Phys. Rev. B.

MWCNTs parameters

Longitudinal modulus $E_{33}^{tension}/E_{33}^{compression}$ (GPa)	687.21/1051.1
Major Poisson's ratio $\nu_{31}^{tension}/\nu_{31}^{compression}$	0.12807/ 0.13686
Longitudinal shear modulus G_{31} (GPa)	204.71
In-plane bulk modulus K_{12} (GPa)	112.11
In-plane shear modulus G_{12} (GPa)	2.0256

Weidt & Figiel (2015), 115: 52, Comp. Sci. Techn.

e.g. C_r bond-stretching constant; C_θ bond-angle variation constant; n - chirality

Matrix behaviour

Strain energy function

$$A_{\mathrm{C}} = A_{\mathrm{C}}\left(\hat{\lambda}_{\boldsymbol{N}}^{(\boldsymbol{i})}, \mathrm{T}, \mathrm{N}_{\boldsymbol{C}}, \alpha\right)$$

Edwards & Vilgis (1986), 27: 483, Polymer

Rejuvenation

$$T_{\mathrm{f}\sigma} = T_{\mathrm{f}\sigma 0} + (T_{\mathrm{f}\sigma\infty} - T_{\mathrm{f}\sigma 0})\left[1-\exp\left(-\frac{\bar{\varepsilon}^{\mathrm{v}}}{\varepsilon_0^{\mathrm{v}}}\right)\right]$$

Buckley et al. (2004), 52: 2355, J. Mech. Phys. Sol.

Adiabatic heating

$$\dot{T} = \frac{1}{\rho c}\left[\bar{\boldsymbol{\sigma}} : \bar{\boldsymbol{D}} - \bar{\boldsymbol{\sigma}}^{\mathrm{b}} : \bar{\boldsymbol{D}}^{\mathrm{e}}\right] - \frac{\varphi \Delta c\, \dot{T}_{\mathrm{f}\sigma}}{c}$$

Buckley et al. (2004), 52: 2355, J. Mech. Phys. Sol.

Values of model parameters

	Epon 828/Jeffamine T403
Shear modulus G (Pa)	0.87e+9
Bulk modulus K (Pa)	3.078e+9
Glass transition temperature T_g (K)	363[a]
Density ρ (kg m ^{3})	1140[a]
Number density of crosslinks N_c (m ^{3})	5.7e+27
Inextensibility factor of network α	0.297
Final fictive temperature $T_{f\sigma\infty}$ (K)	372
Linear viscoelastic relaxation time τ_0 (s)	2.02e+6
Rejuvenation strain range ε_0^v	0.339

Weidt & Figiel (2015), 115: 52, Comp. Sci. Techn.

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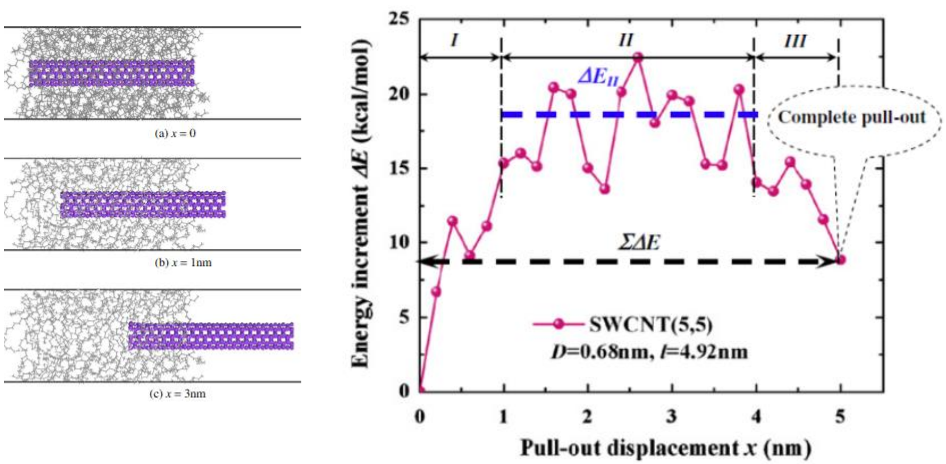
Interface behaviour

CNT pull-out via MD



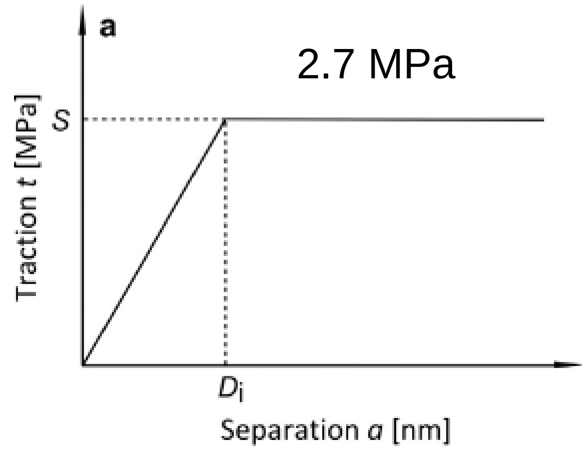
Li et al. (2011), 50: 1854, Comp. Mat. Sci.

$$F_{\max}^{II} = \frac{\langle \Delta E^{II} \rangle}{\langle \Delta x^{II} \rangle}$$

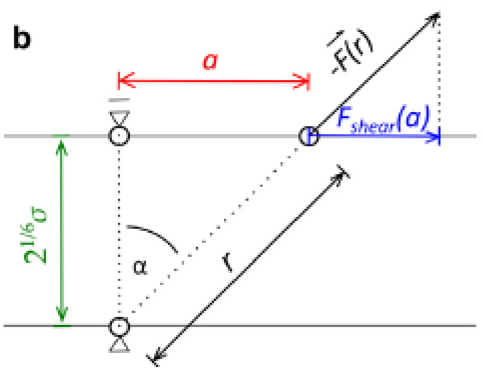
$$S = \frac{F_{\max}^{II}}{\pi d l}$$

$$r^2 = a^2 + \left(2^{1/6}\sigma\right)^2$$

Tangential traction-separation law



Weidt & Figiel (2015), 115: 52, Comp. Sci. Techn.



$$F(r) = 4\frac{\varepsilon}{r}\left[12\left(\frac{\sigma}{r}\right)^{12} - 6\left(\frac{\sigma}{r}\right)^{6}\right]$$

$$F_{shear} = -F\sin\alpha \text{ with } \alpha = \arccos\left(\frac{2^{1/6}\sigma}{r}\right) \quad \text{and} \quad r^2 = a^2 + \left(2^{1/6}\sigma\right)^2$$

$$F_{shear}(a) = -4\frac{\varepsilon a}{a^2 + 2^{1/3}\sigma^2}\left[12\frac{\sigma^{12}}{(a^2 + 2^{1/3}\sigma^2)^6} - 6\frac{\sigma^6}{(a^2 + 2^{1/3}\sigma^2)^3}\right]$$

$$D_i\left(F_{shear}^{\max}(a)\right) = 0.225nm$$

Weidt & Figiel (2015), 115: 52, Comp. Sci. Techn.

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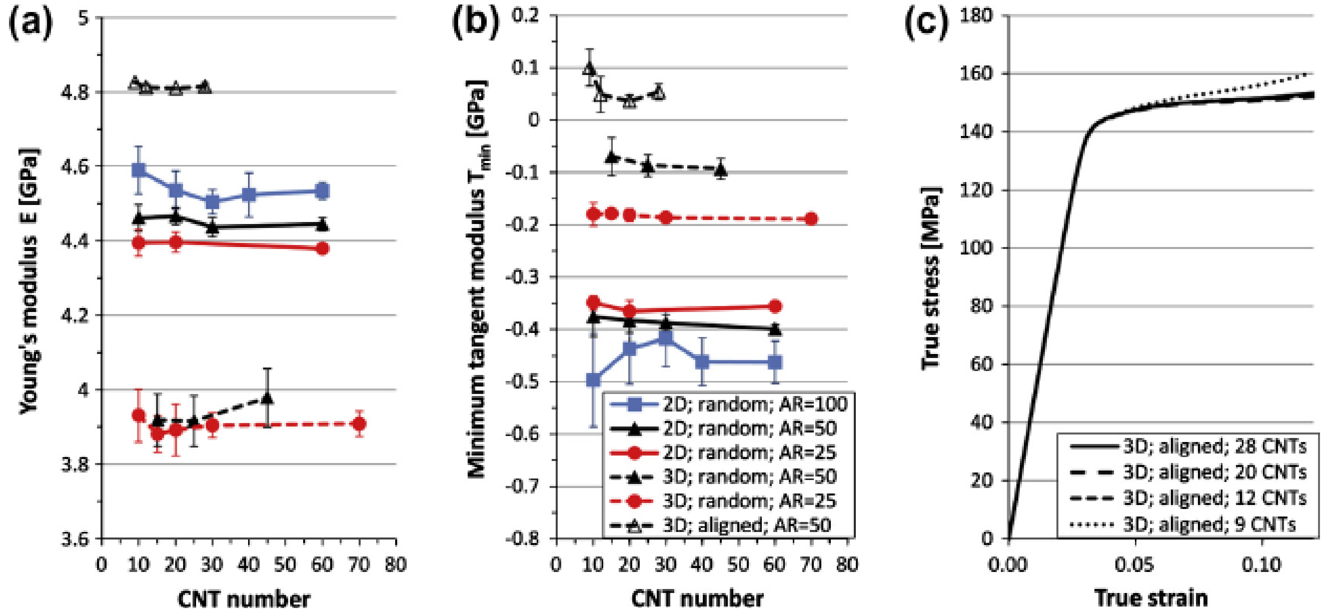
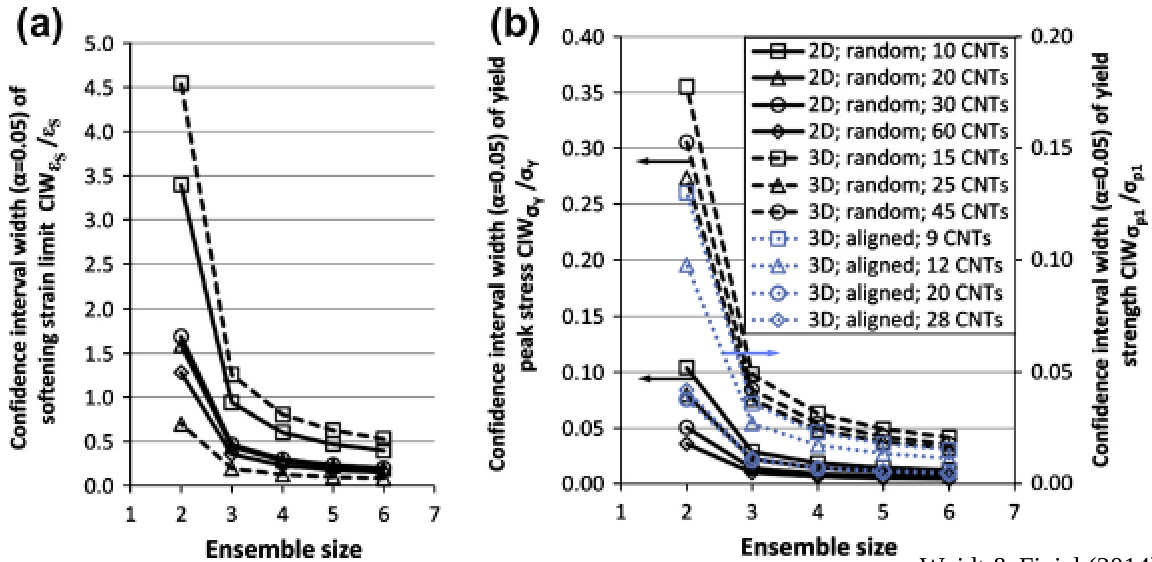
RVE size:

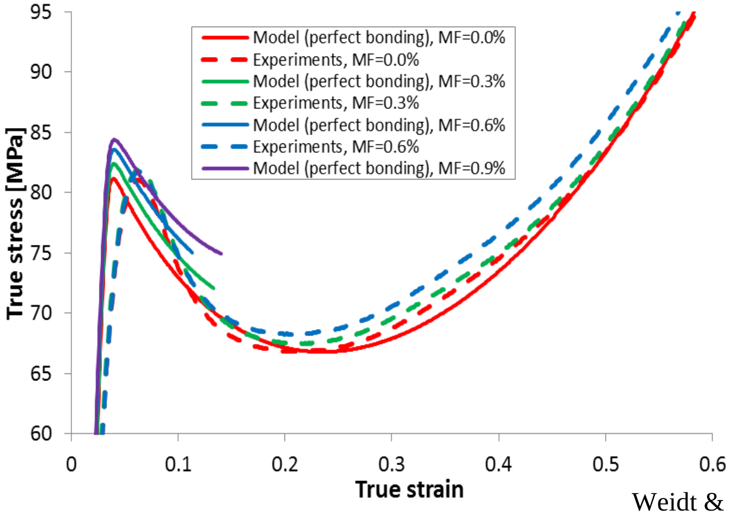


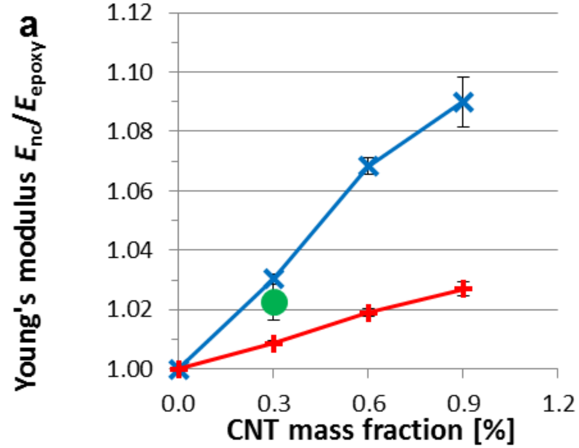
Ensemble size:

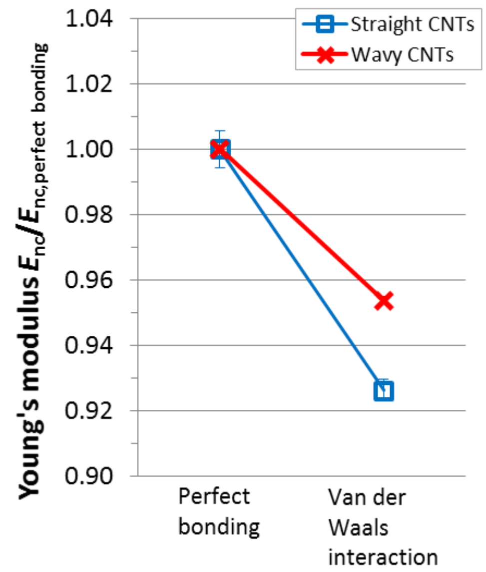


Weidt & Figiel (2014), 82: 298, Comp. Mat. Sci.

Stress-strain rate response, and related parameters



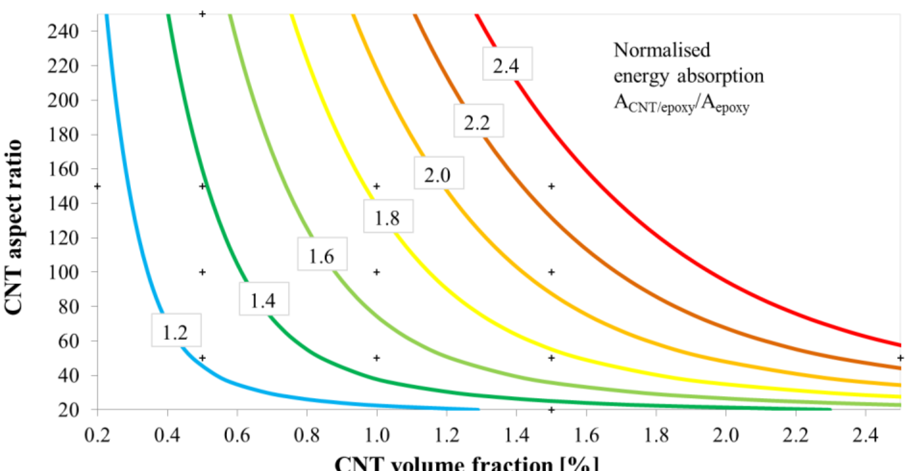




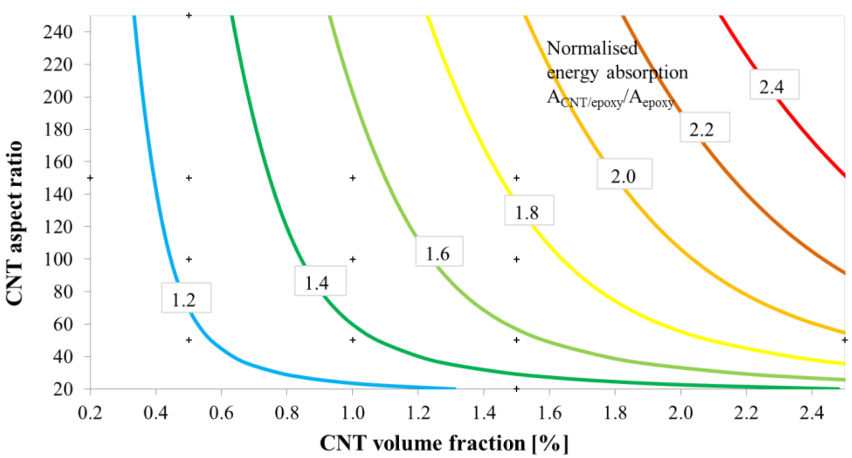
Weidt & Figiel (2015), 115: 52, Comp. Sci. Techn.

Energy absorption

Quasi-static rate (1×10^-3 s^-1)



Impact rate (1×10^3 s^-1)



Weidt & Figiel (2013), In. Njuguna (Ed.), Structural Nanocomposites, 207-224, Springer, 2013.

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Concluding remarks

- Computationally-efficient & accurate, multiscale approach can assist in the optimisation of processing and property enhancements for polymer nanocomposites

- Further work ongoing on:
  - Linking with molecular simulations to account more *accurately* for nanoparticle functionalization & nanoparticle-polymer interactions
  - Description of nanoparticle functionalization-related *uncertainty*
  - Computational efficiency enhancement for localisation-homogenisation scheme through model *reduction* and parallel processing
  - Incorporation of *non-mechanical fields* (e.g. thermal, electric) into the scheme

Acknowledgements

- Dr. C. Pisano, Dr. D. Weidt (University of Limerick, Ireland)
- Prof. P. Buckley (University of Oxford, UK)
- Prof. F. Dunne (Imperial College London, UK)
- Dr. P. Spencer (University of Bradford, UK)
- Dr. G. Menary (Queen's University Belfast, UK), Dr. K. Soon, Dr. R. Rajeev (formerly at Queen's University Belfast, UK)
- Prof. A. Galeski (CMMS Lodz, Poland)

- Engineering and Physical Sciences Research Council (EPSRC), UK
- Materials & Surface Science Institute, University of Limerick, Ireland
- Irish Research Council (IRC)
- Irish Centre for High-End Computing (ICHEC)
- National Science Centre, Poland