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Foster, RJ orcid.org/0000-0002-5337-3615, Hine, PJ, Bonner, MJ et al. (1 more author) (2008) The incorporation of carbon nanofibres to enhance the properties of hot compacted self-reinforced single polymer composites. In: Proceedings of the 13th European Conference on Composite Materials (ECCM 13). ECCM 13: The 13th European Conference on Composite Materials, 02-05 Jun 2008, Stockholm, Sweden. European Society for Composite Materials .

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The Incorporation of Carbon Nanofibres to Enhance the Properties of Hot Compacted Self-Reinforced Single-Polymer Composites

R J Foster, P J Hine, M J Bonner & I M Ward
ECCM 13 2-5th June 2008

Development of enhanced polymers

“COMMODITY” POLYMERS

Cheap and easy to manufacture

Limited mechanical properties at elevated temperatures

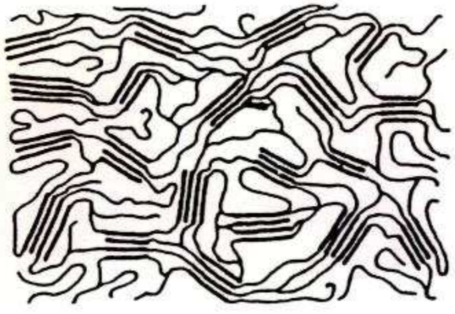
Control of molecular orientation and morphology

Structure-Property Relationships between experimental results and theoretical predictions

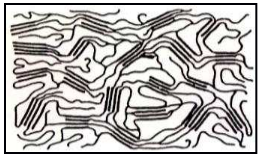
Add a reinforcement usually glass fibres:

Control orientation and fibre length

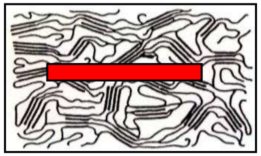
250 GPa



1 GPa



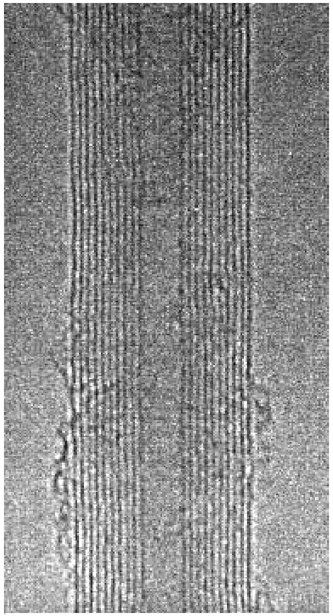
Unfilled PE 1 GPa



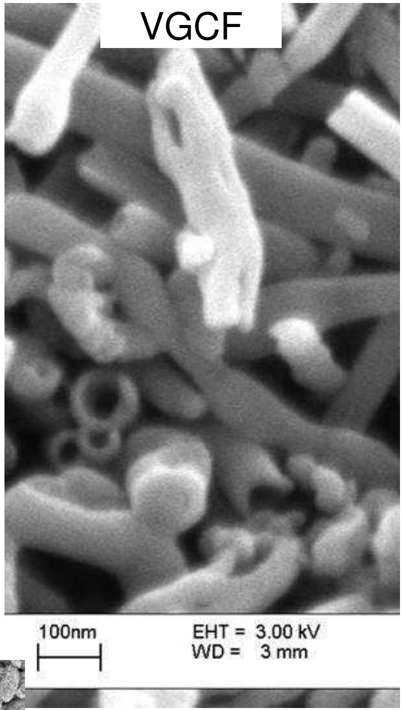
30% w/w glass filled PE: aligned fibres 8 GPa

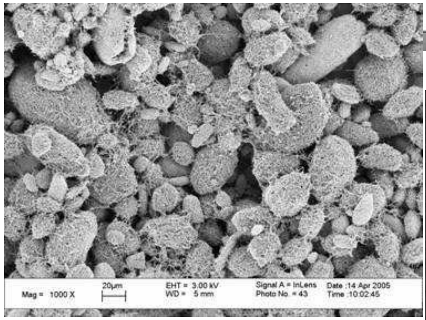
Carbon nanotubes and nanofibres

- Seamless cylinders of graphene
- Carbon-carbon bond – exceptional strengths & mechanical resilience
- Vapour Grown Carbon Fibres's (VGCF/CNF)
  - Seeded in vapour, entangled mass
  - Relatively inexpensive.
- Highly Entangled fibre assembly - need to disentangle whilst retaining length for best mechanical properties
- Potential blending routes include high shear mixing, solvent dispersion, ball-milling, compatiblisers and ultrasound

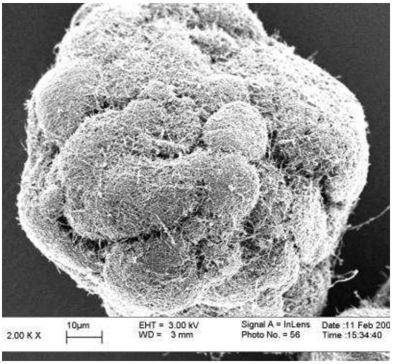


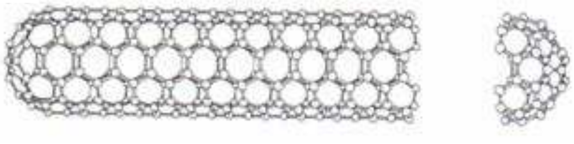
MWNT





VGCF





SWNT

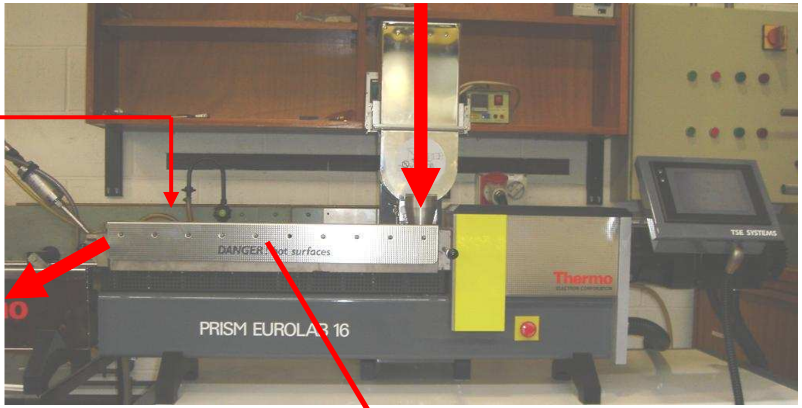
High shear mixing

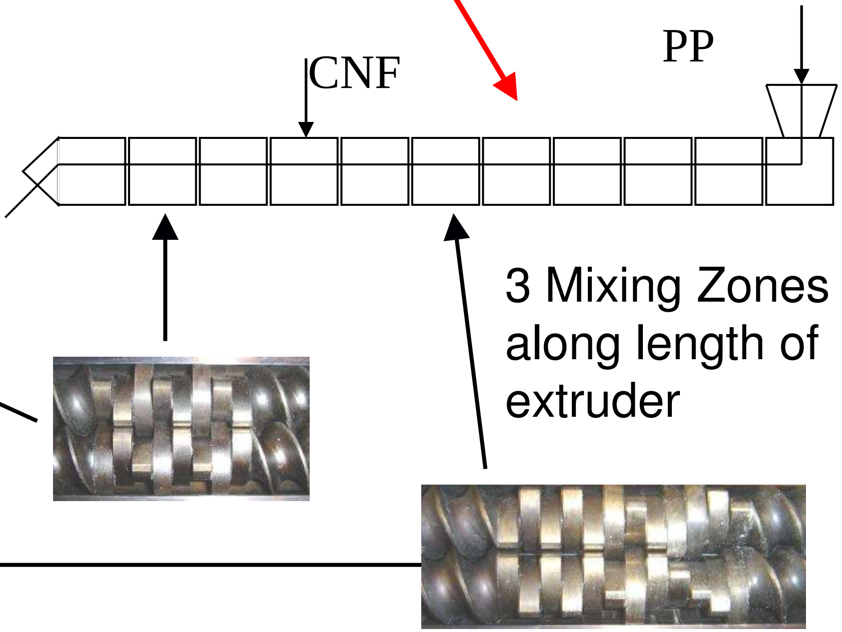
Prism Twin Screw Extruder

Introduce Carbon Nanofibres (CNF) at end of 1st Extrusion (5% by volume)

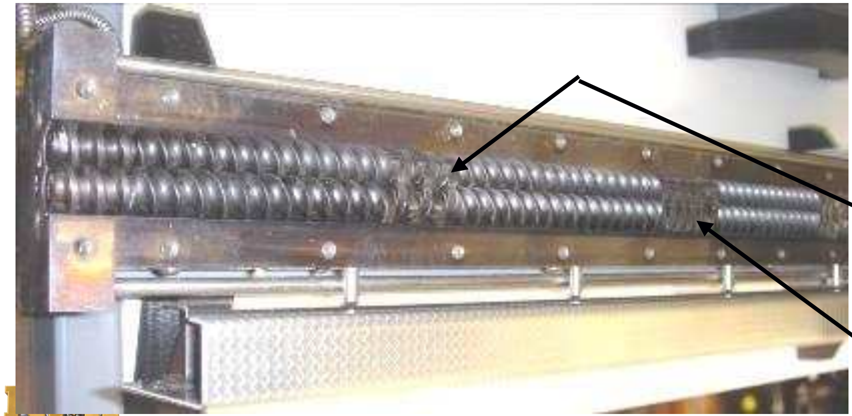
Removal of material in pellet form after each extrusion –compression moulded sheet for properties testing

Re-introduce material into extruder for a 2nd & 3rd extrusion (4 & 7 Mixes)



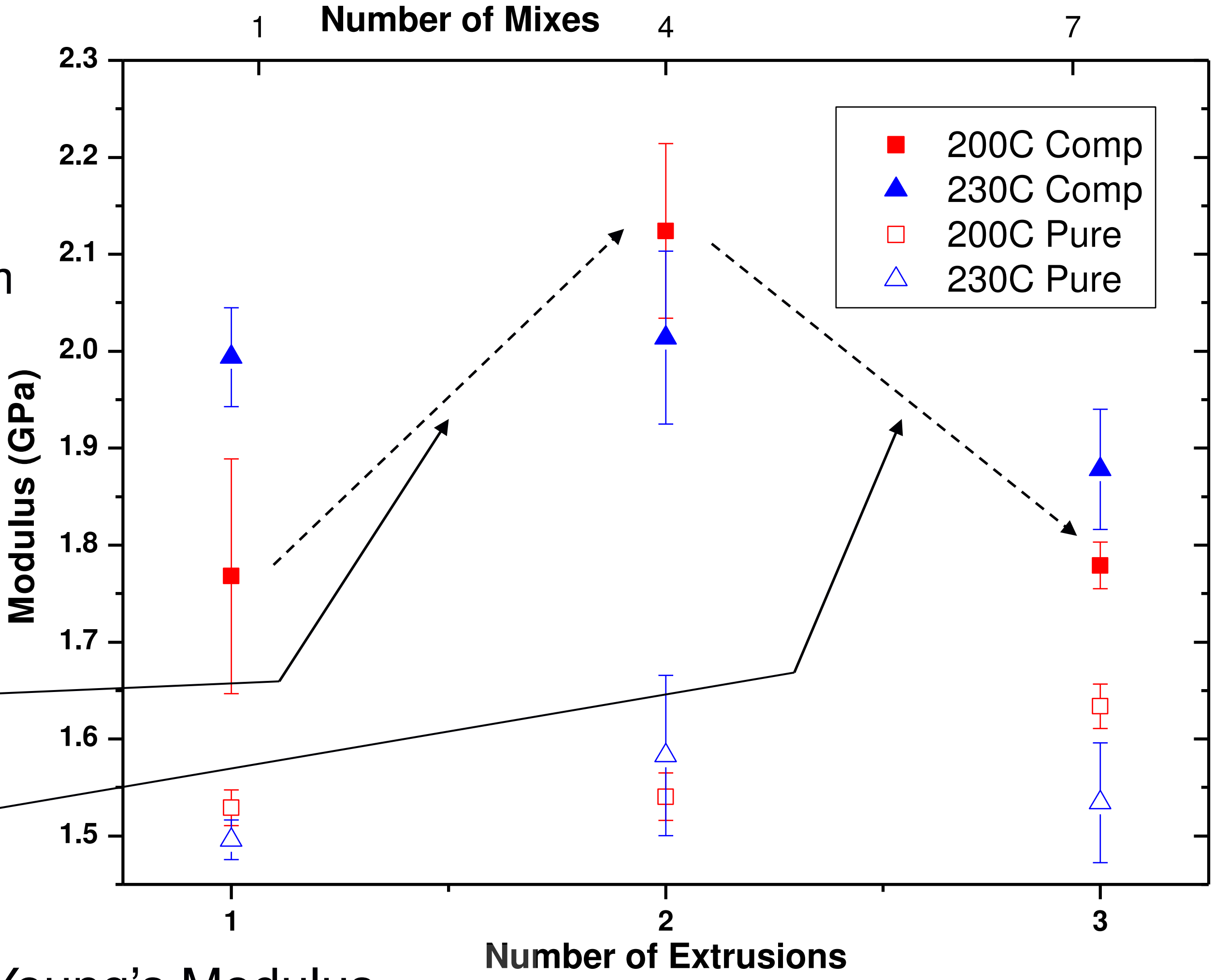


3 Mixing Zones along length of extruder



Properties of blended material

- Both Blending Temperatures 5% CNF by volume
- Isotropic Compression moulded sheets made from pelletised material
- Static tensile testing
- Young's modulus goes through clear peak after 4 mixes
- Increase attributed to improved dispersion
- Decrease attributed to reduction in CNF length

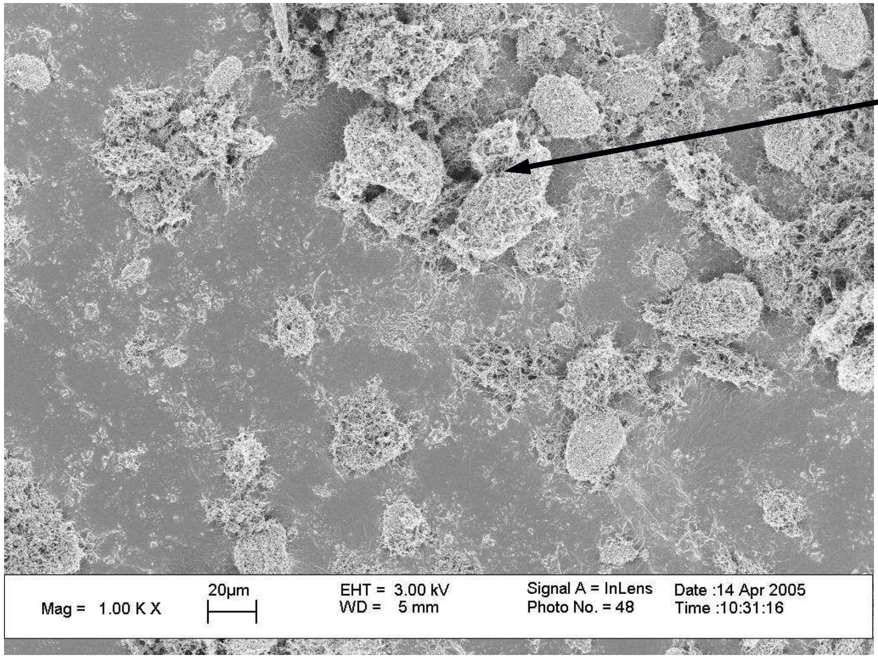


~37% increase in Young's Modulus (1.55GPa to 2.12GPa)

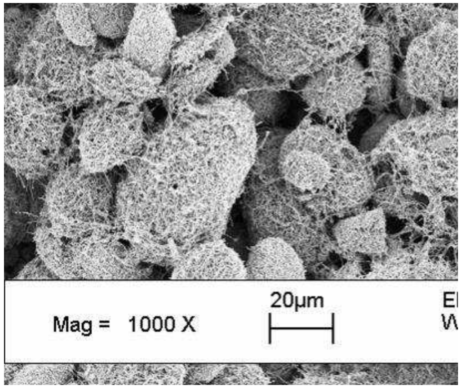
Isotropic Compression Moulded Sheets

A single mix

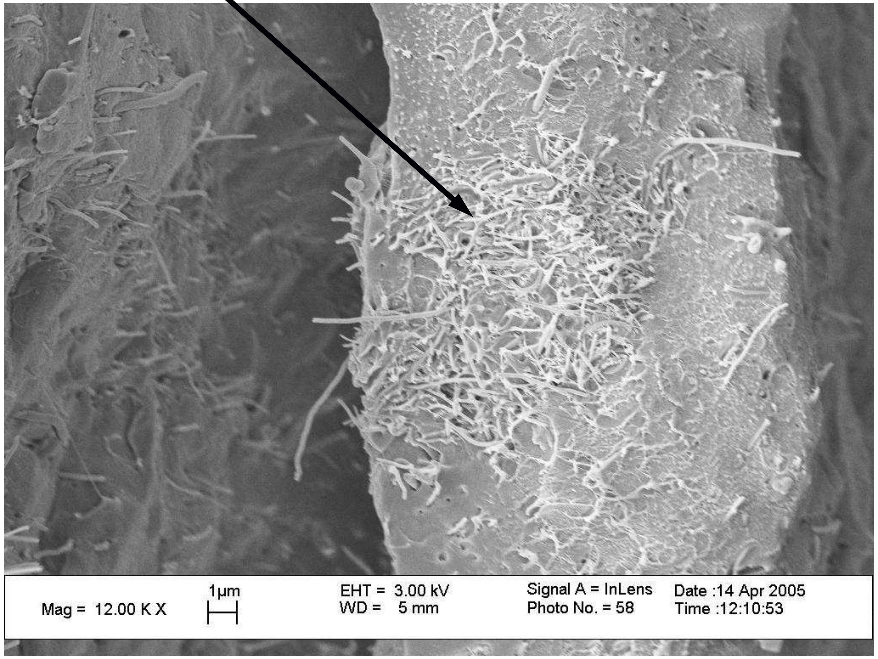
- Burning off PP matrix from material mixed once shows ball-like structures intact, similar to the as-received CNF
- Freeze fracture of composite sheet from same material shows regions of un-wetted fibres



CNF blended at 200°C, 1 mix (1 extrusion)

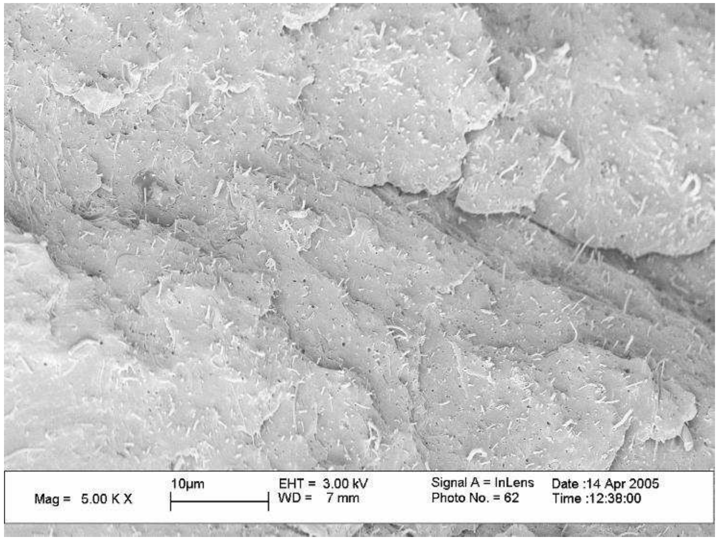


As Received CNF

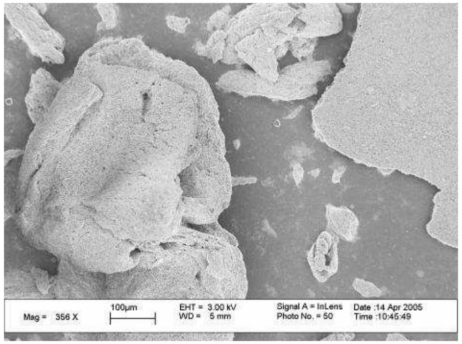


Freeze Fracture Sample of Compression Moulded Sheet from material blended at 200°C, 1 mix (1 extrusion)

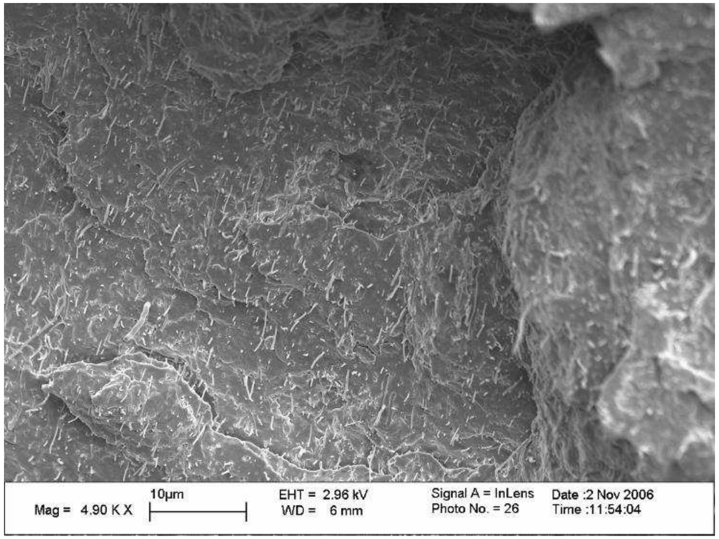
More mixes….



Freeze Fracture Sample of Compression Moulded Sheet from material blended at 200°C, 7 mixes (3 extrusions)



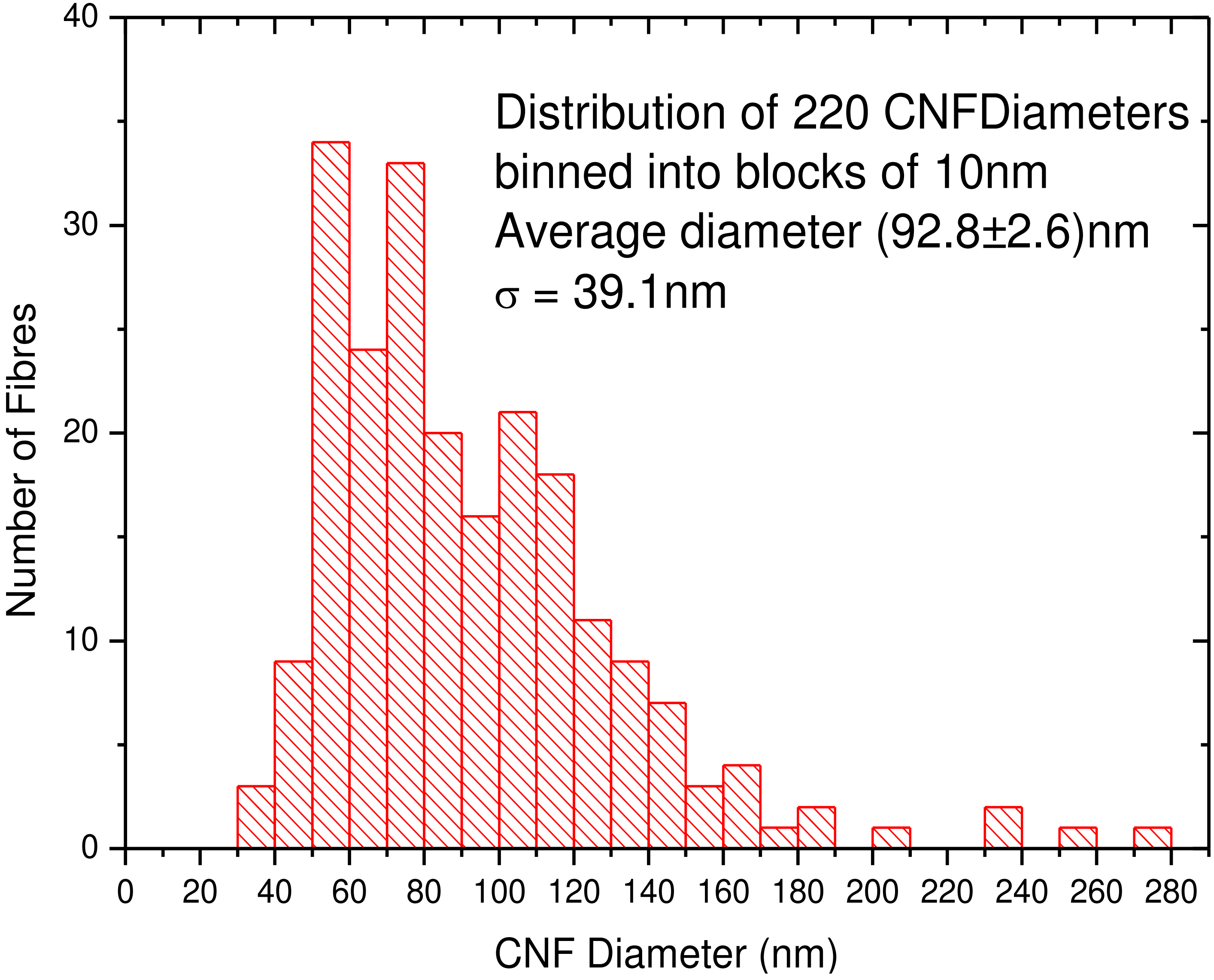
CNF 'Mats' – reaggregated fibres (4, 7 Mixes)



Freeze Fracture Sample of Compression Moulded Sheet from material blended at 200°C, 4 mixes (2 extrusions)

- Burning off matrix for material mixed more than once leads to re-aggregation of fibres –no direct information about blending process
- Can infer that material must be well mixed and fibres must have been separated in order for them to re-aggregate
- Confirmed by freeze fracture of composite sheet
- Thus increase in Young's modulus going from 1 mix to 4 mixes is due to improved dispersion

Diameter measurement



Distribution of 220 CNFDiameters
binned into blocks of 10nm
Average diameter (92.8±2.6)nm
σ = 39.1nm

Dynamic Light Scattering

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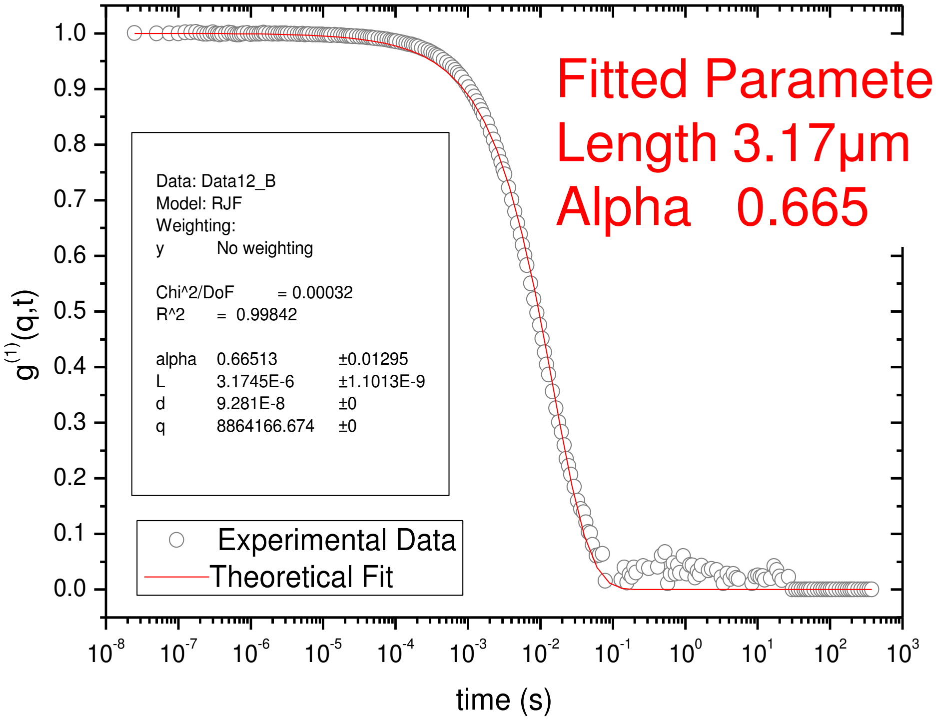
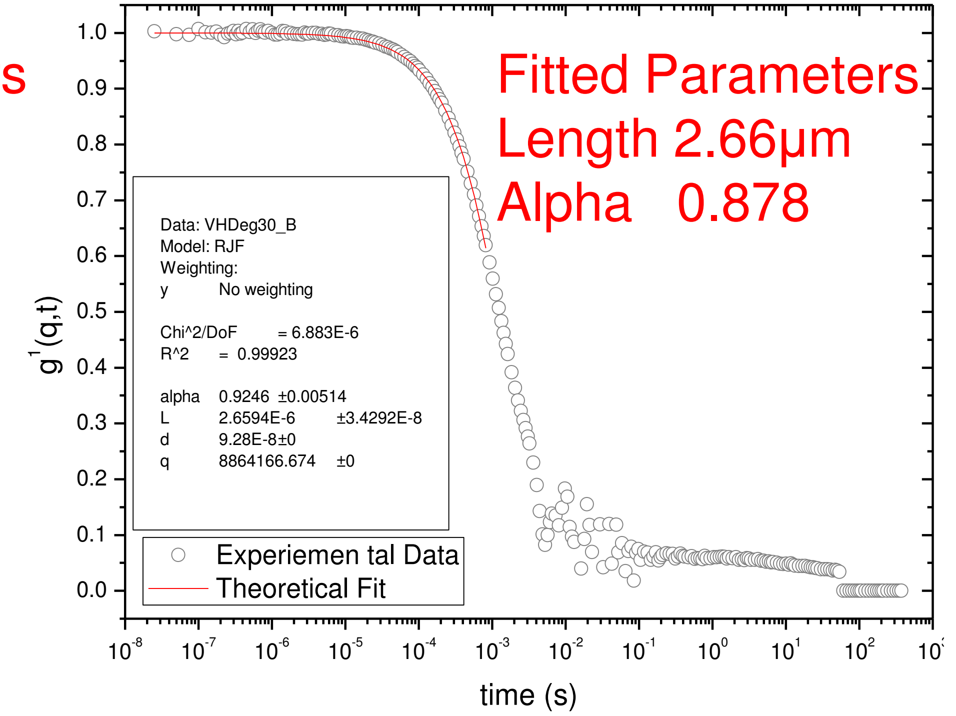
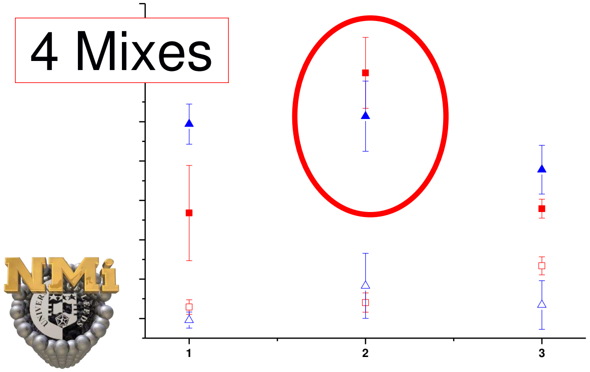


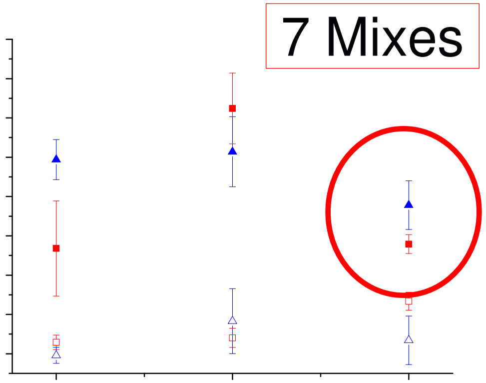
Fitted Parameters
Length 3.17μm
Alpha 0.665



Fitted Parameters
Length 2.66μm
Alpha 0.878



DLS indicates a reduction in CNF length as the number of mixes increases



The Cox-Krenchel model

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Composite Modulus modelled using Cox-Krenchel equation (modification of the rule of mixtures):

$$E_C = \eta_0 \eta_l V_f E_f + (1 - V_f) E_m$$

V_f = Volume fraction of fibres, E_f = Young's Modulus of fibres, E_m = Young's Modulus of matrix

η_0 is orientation efficiency factor:

$$\eta_0 = \sum_n a_n \cos^4 \theta_n \quad \text{where} \quad \sum_n a_n = 1$$

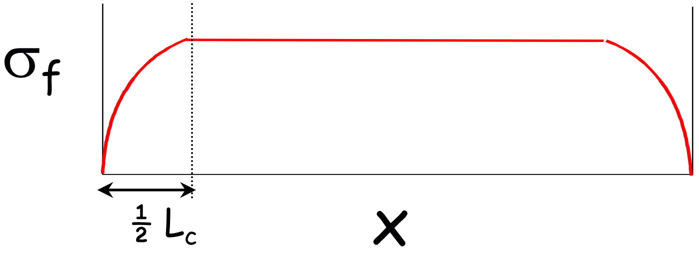
For 3D: η_0 = 1/5 and for 2D: η_0 = 3/8

η_l is length efficiency factor (Cox Shear Lag factor):

$$\eta_l = 1 - \frac{\tanh(\beta l/2)}{\beta l/2}$$

Where l is the length of the fibres, and β is given by:

$$\beta = \left(\frac{2\pi G_m}{E_f A_f \log_e(R/r)} \right)^{\frac{1}{2}}$$



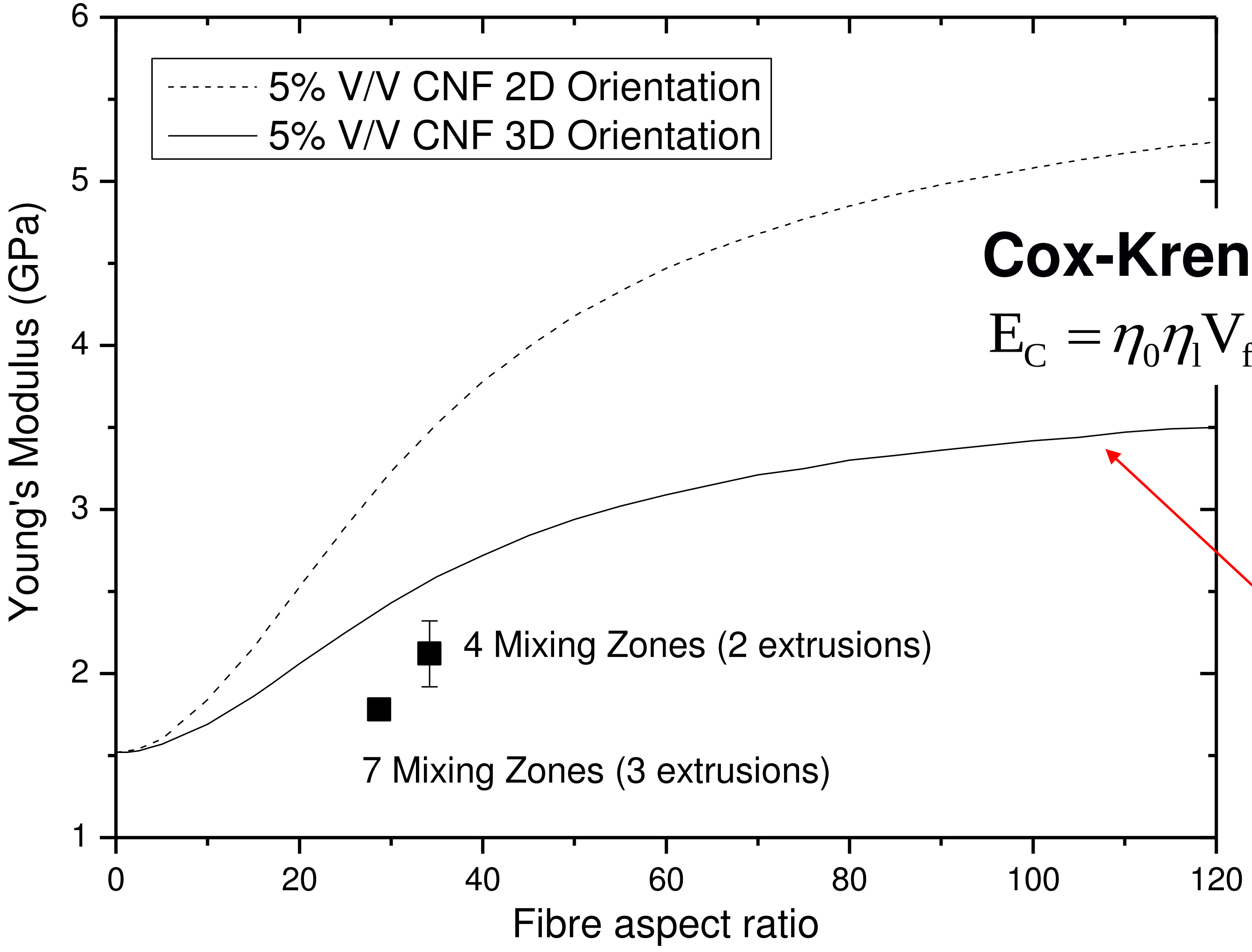
Critical Parameters -fibre length, fibre diameter and volume fraction

Folkes, M. J., "Short Fibre Reinforced Thermoplastics". 1985, John Wiley & Sons.

Cox-Krenchel modelling

Effect of fibre length upon the modulus of a PP/CNF composite sheet comparing 2D and 3D randomly oriented fibres

Isotropic Sheets



Cox-Krenchel Model

$$E_C = \eta_0 \eta_l V_f E_f + (1 - V_f) E_m$$

C-K Model overestimates composite modulus

Amount of nanofiller

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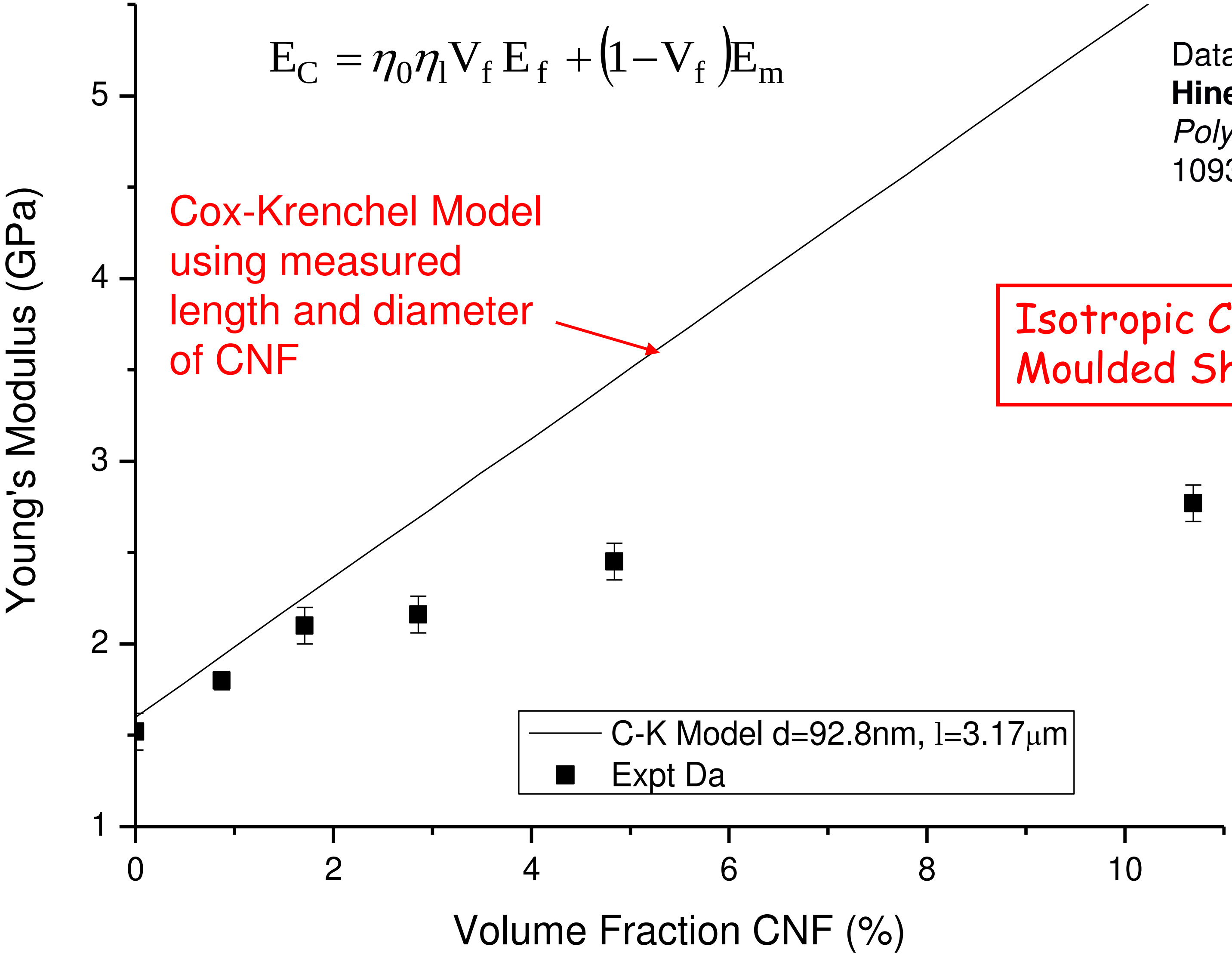


$$E_C = \eta_0 \eta_l V_f E_f + (1 - V_f) E_m$$

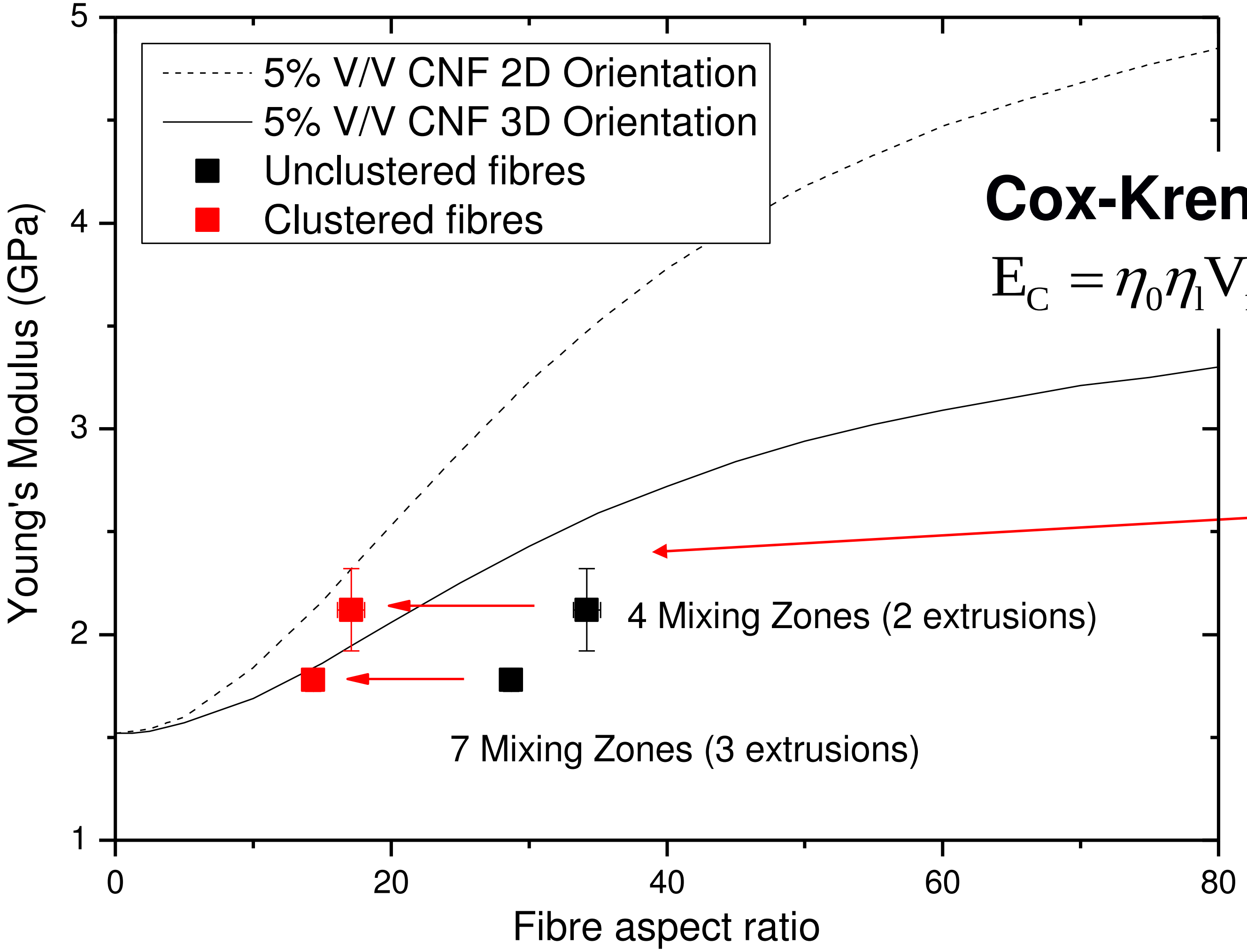
Cox-Krenchel Model using measured length and diameter of CNF

Data taken from **Hine, P., et al,** *Polymer*, **46,** (2005), 10936

Isotropic Compression Moulded Sheets

Cox-Krenchel modelling

Effect of fibre length upon the modulus of a PP/CNF composite sheet comparing 2D and 3D randomly oriented fibres

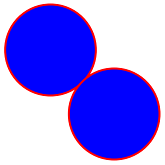


Isotropic Sheets

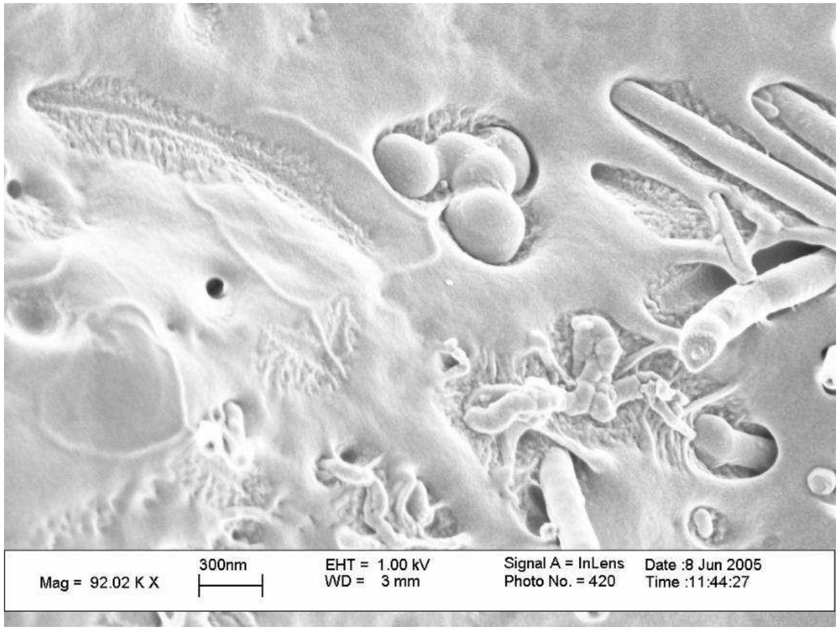
Cox-Krenchel Model

$$E_C = \eta_0 \eta_l V_f E_f + (1 - V_f) E_m$$

Clustering of fibres can explain discrepancy between model and expt

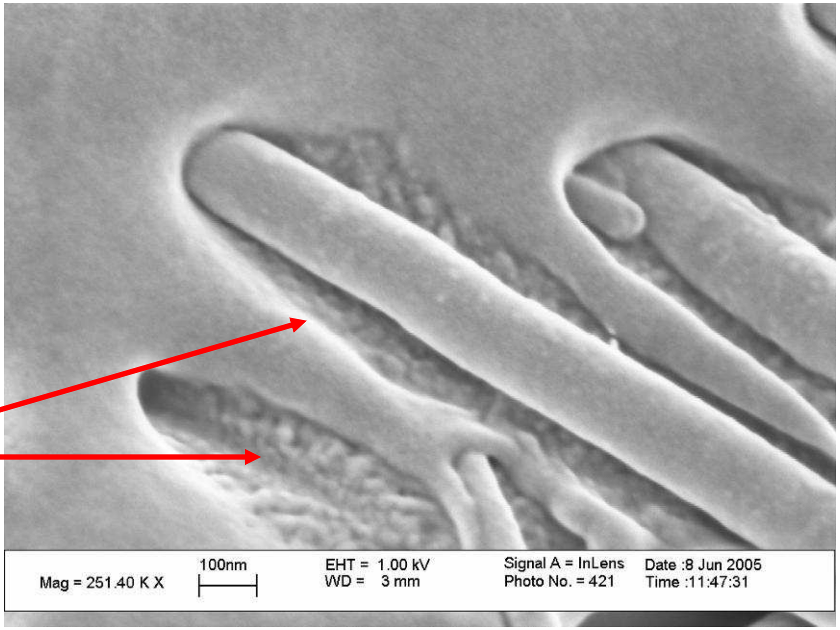


Morphology



SEM image of freeze fracture from isotropic sheet shows CNF can modify the local microstructure forming transcrystalline layer

Transcrystalline layer (row aligned molecules nucleated on CNF)



Temperature performance

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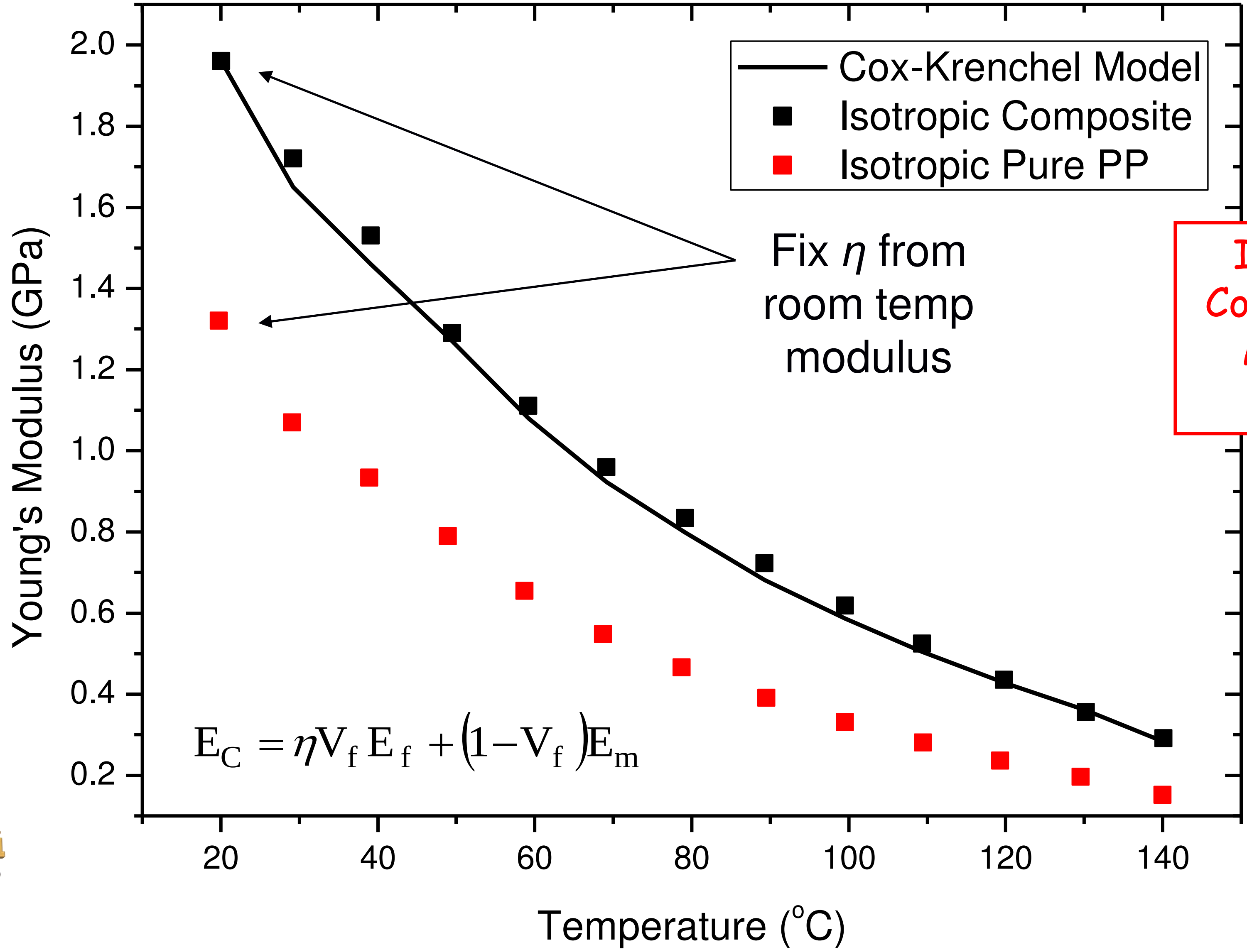


Fix η from room temp modulus

$$E_C = \eta V_f E_f + (1 - V_f) E_m$$

Isotropic Compression Moulded Sheets

Hot compaction

Take an array of oriented polymer fibres or tapes.

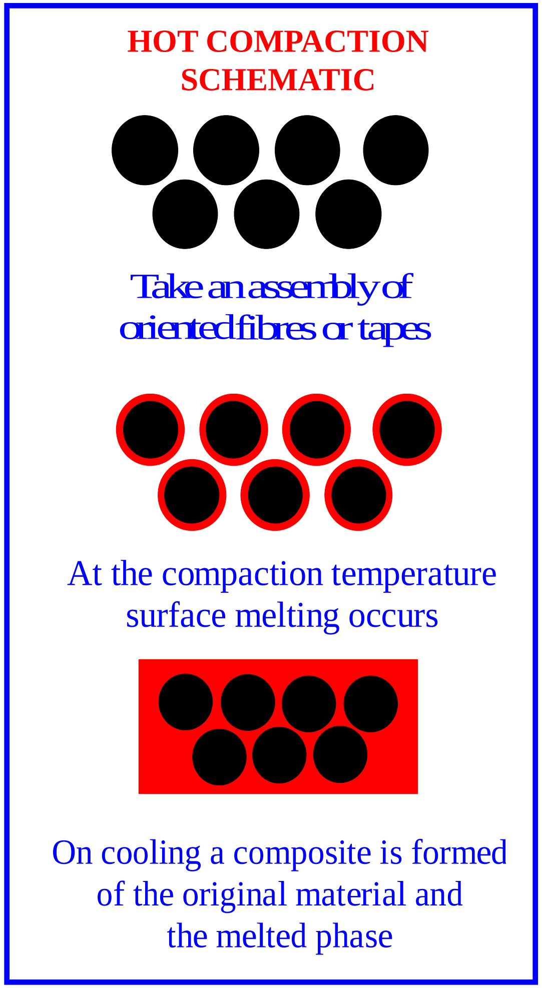
↓

Process at a suitable temperature to melt only the skin of the oriented elements and keep the oriented core.

↓

On cooling the melted material freezes to bind the oriented elements together forming a single polymer composite.

Draw ratio of tapes (level of molecular orientation) controls final properties.



HOT COMPACTION SCHEMATIC

Take an assembly of oriented fibres or tapes

At the compaction temperature surface melting occurs

On cooling a composite is formed of the original material and the melted phase

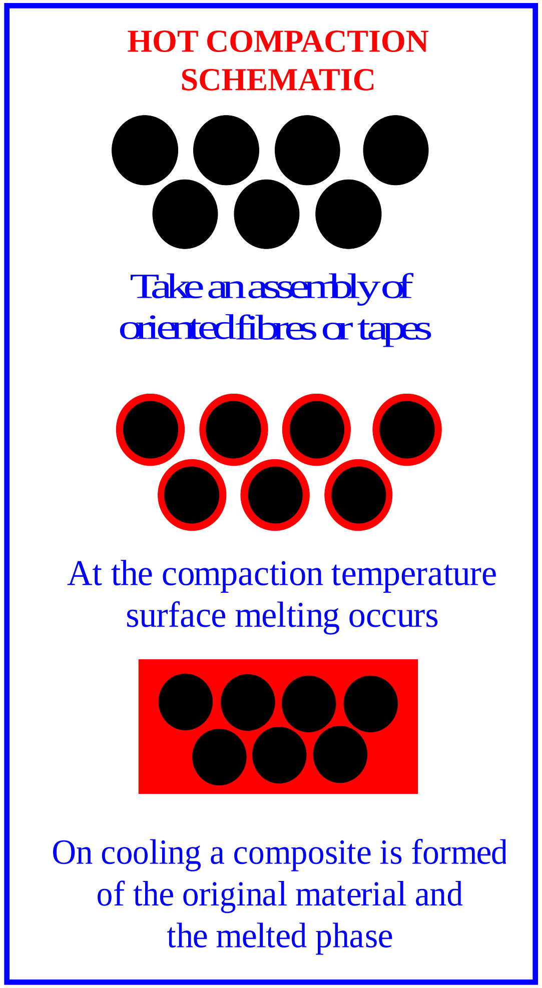
Ward, I. M., Hine, P. J., *Polymer*, **45**, (2004), 1423

Hot compaction

Nike Contour Shinguards

Automotive Undertray

Samsonite Suitcases



HOT COMPACTION SCHEMATIC

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Ward, I. M., Hine, P. J., *Polymer*, **45**, (2004), 1423

Laminate Modelling

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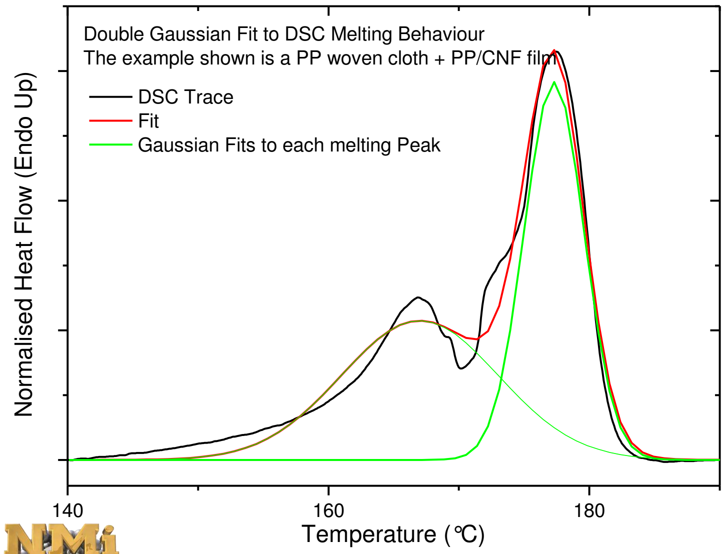
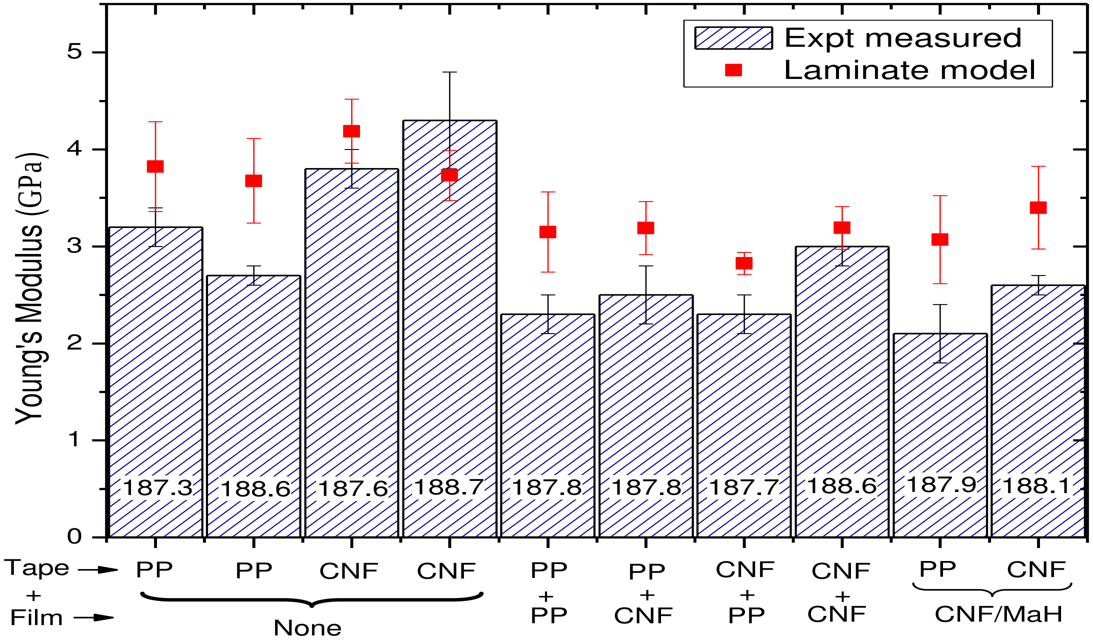
Modulus of laminate structure can be predicted from modification of the rule of mixtures:

$$E_{\mathrm{Composite}} = \left(\frac{\mathrm{Vol}_{\mathrm{Oriented}}}{2}\right)E_{\mathrm{oriented}} + \left(1-\frac{\mathrm{Vol}_{\mathrm{Oriented}}}{2}\right)E_{\mathrm{Matrix}}$$

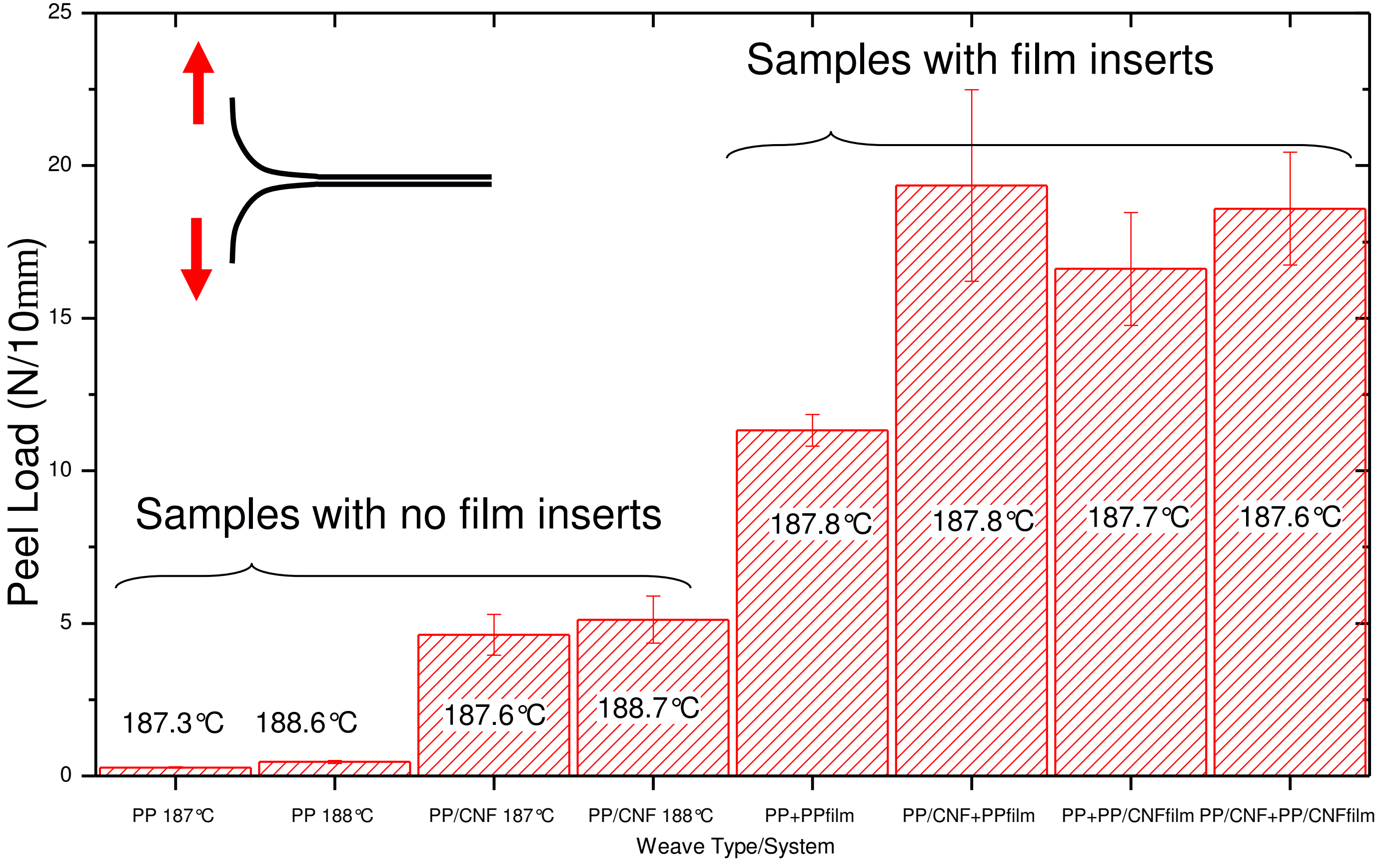
Measure E_{oriented} (tapes) and E_{matrix} (isotropic)

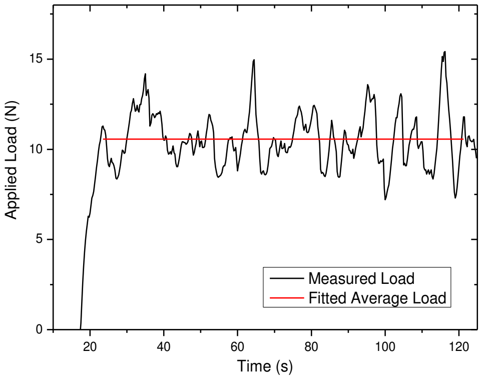
Use DSC to determine the amount of material in each phase





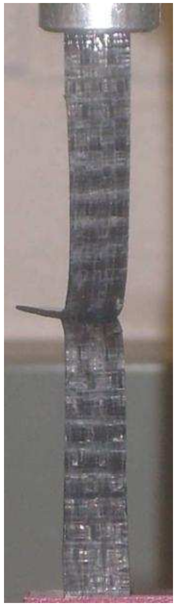
Peel Strength (Delamination)





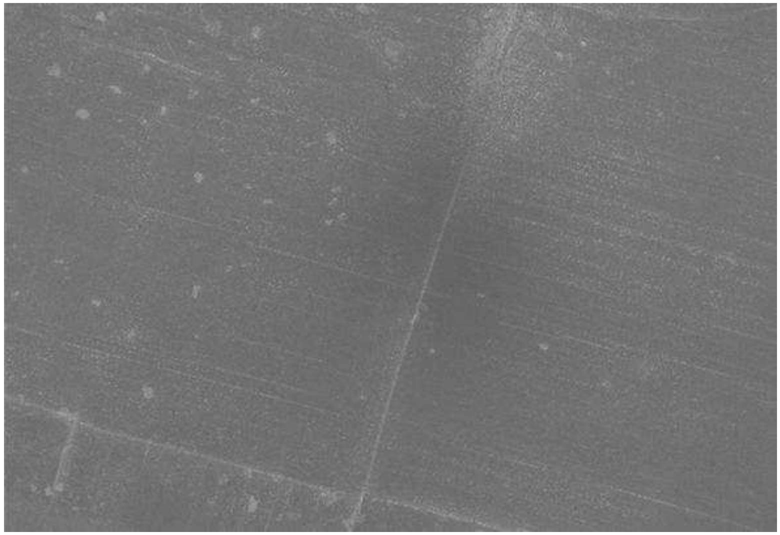
10mm wide strips pulled apart at 80mm/min

Force–time behaviour determined



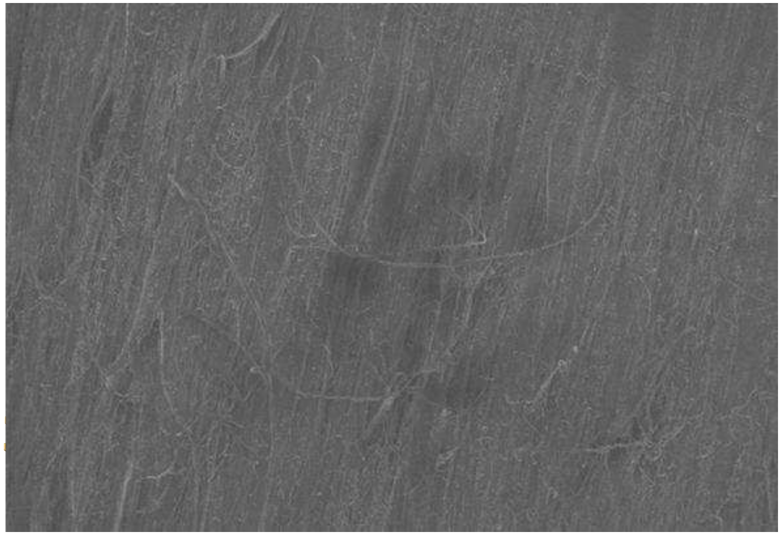
- CNF dramatically improves Peel Strength of PP (from <0.5N to ~5N)
- HCPP with PP film increases Peel force by order of magnitude (~11N)
- Hot compacted nanocomposite shows further improvement (~18N)
- Surprisingly doesn’t matter into what phase CNF are incorporated

Fracture Surfaces

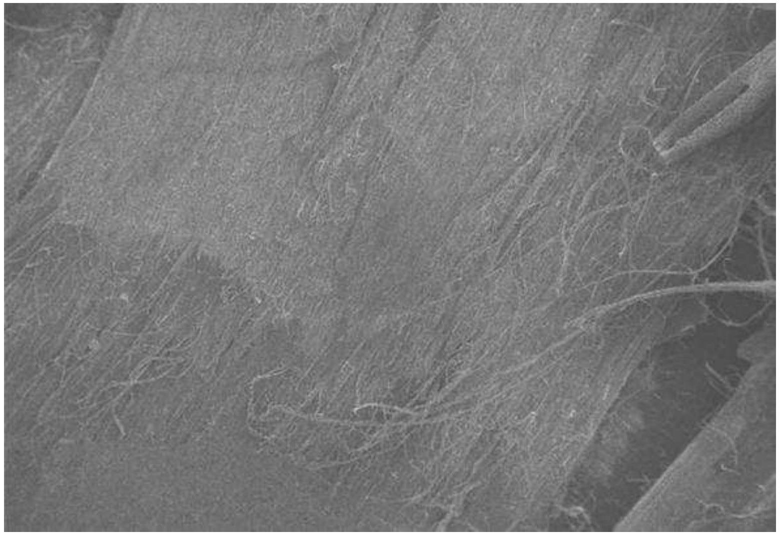


PP with no film inserts

PP/CNF with no film insert



PP with PP film inserts



PP with PP/CNF film inserts

Conclusions

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- Polypropylene-CNF nanocomposite material successfully blended using high shear mixing. Peak in properties after 4 mixes.
- DLS and SEM analysis used to measure CNF length, diameter and dispersion – modelling gives insight into structure-property relationship
- Improved temperature performance of nanocomposite material
- Nanocomposite has been drawn and hot compacted to produce CNF reinforced single-polymer composites.
- Interlayer adhesion (peel force) of single-polymer composites improved dramatically by incorporation of CNF. Film layers of PP and PP/CNF allow further improvement.
- SEM has identified differences in the fracture surfaces. Ongoing investigation into full effect of CNF.

The authors would like to thank the Nanomanufacturing Institute for funding this study