Welsh Centre for Printing and Coating

SWANSEA UNIVERSITY
PRIFYSGOL ABERTAWE

College of Engineering

Stretchable inks for wearable applications

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EPSRC
Engineering and Physical Sciences Research Council

ESF
Llywodraeth Cymru
Welsh Government
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Cronfa Gymdeithasol Ewrop
Europe & Wales: Investing in your future
European Social Fund

Stretchable inks for wearable applications

Content

- WCPC
- Requirements
- Printing onto fabric
- Ink formulation
- Examples of performance of stretchable inks
- Advanced Rheology for formulation and process control
- Scaling up to volume production

Printing as a manufacturing process

Centre of excellence
for
Printing, Packaging and Coating

- World leading fundamental research
- Underpinning science of the printing process
- Comprehensively equipped open access centre
- Technology transfer
- Education and training

Inks for wearable technology

- Bend and stretch to allow garment to
  - conform to the wearers body
  - accommodate without impedying movement
- Flexing and stretching must have minimal or predictable effect on function
- Washable
- Liquid ink
  - Must be printable

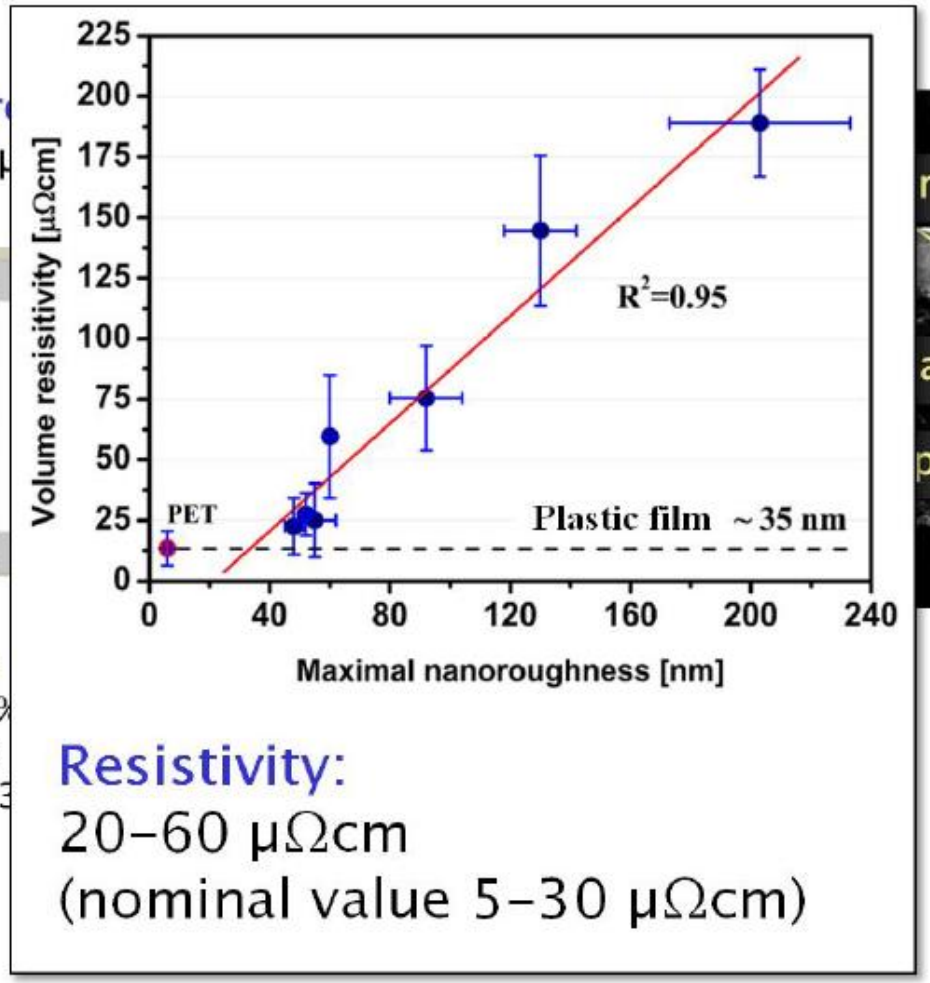
Printing large areas onto fabric

- Print onto polymer and heat transfer to fabric
  - Smooth substrate
  - Flex but not stretch
  - Flex and stretch (substrate provides elastic recovery)
- Print direct to fabric
  - Surface roughness
  - Absorption
  - Similar problems to paper
- Fabric could
  - Form part of the electrical component
  - Channel fluids by local printed treatments

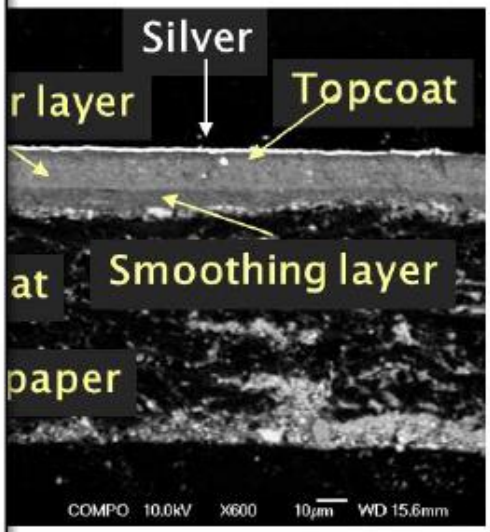
Roughness vs Conductivity

Ag comb structur
- Line width 185 µ
- Gap 595 µm

Silver ink for inkjet:
Silver content 20 wt%
Viscosity 10–13 cps
Surface tension 27–3



Resistivity:
20–60 µΩcm
(nominal value 5–30 µΩcm)



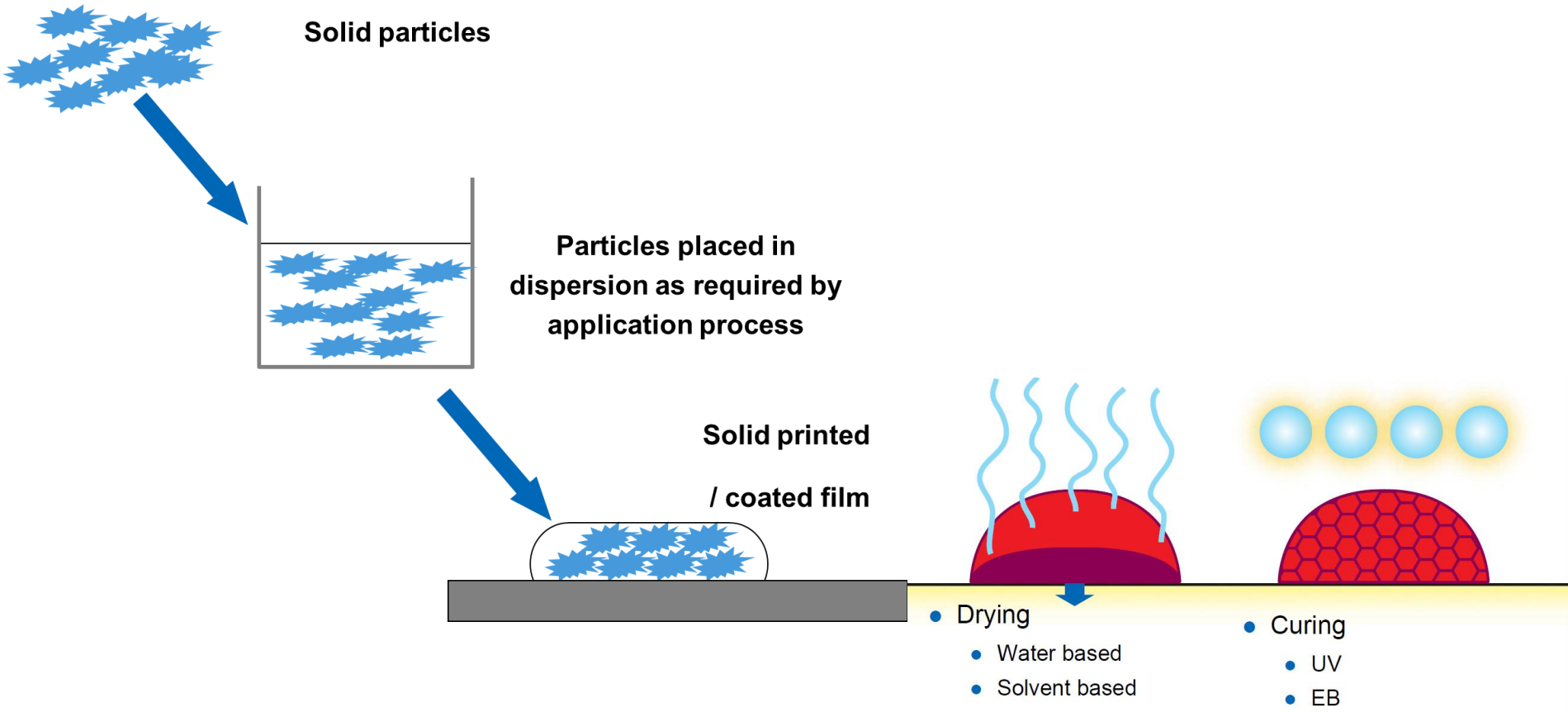
Määttänen, et al., Colloid Surfaces A 367 (2010) 76–84

Martti Toivakka 2017

Ink Formulation

- Resin/binder
  - Solvent cure – evaporating solvent reduces volume
  - UV – cures to a solid of same volume as when wet
- Active materials
  - Solid Particles
  - Long chain polymers
- Solvent
  - Dissolve resin
  - Adjust flow properties
- Additives

Ink Formulation

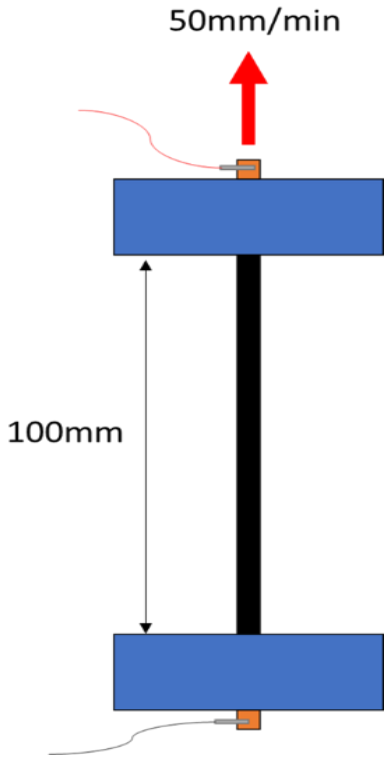


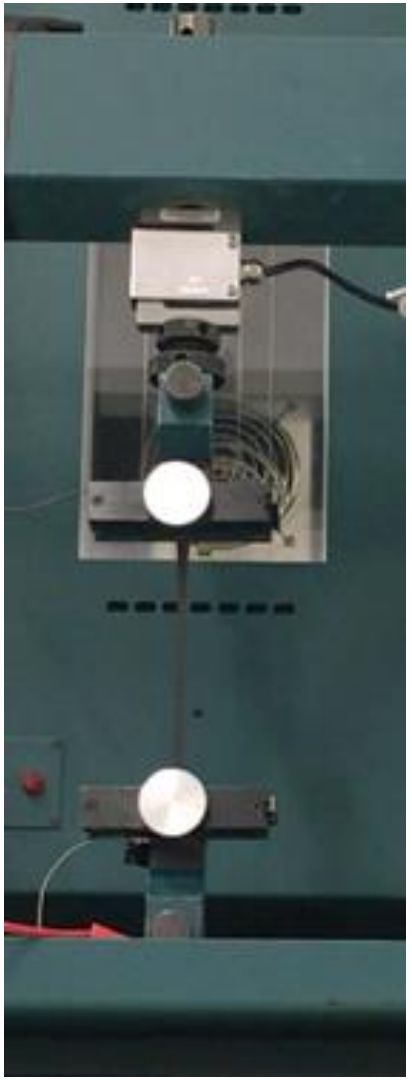
Formulation

- Flexible/stretchable resin
- Solid particles
  - Nano particles e.g. Carbon black, silver nano wires, copper
  - Flakes e.g. Graphite, silver
    - Larger the flake
      - More conductive the ink
      - Rougher the print
- Increasing Solid loading:
  - Lowers resistance
  - Reduces flexibility/stretchability
  - Reduces Printability

Stretchability of a conductive silver and carbon

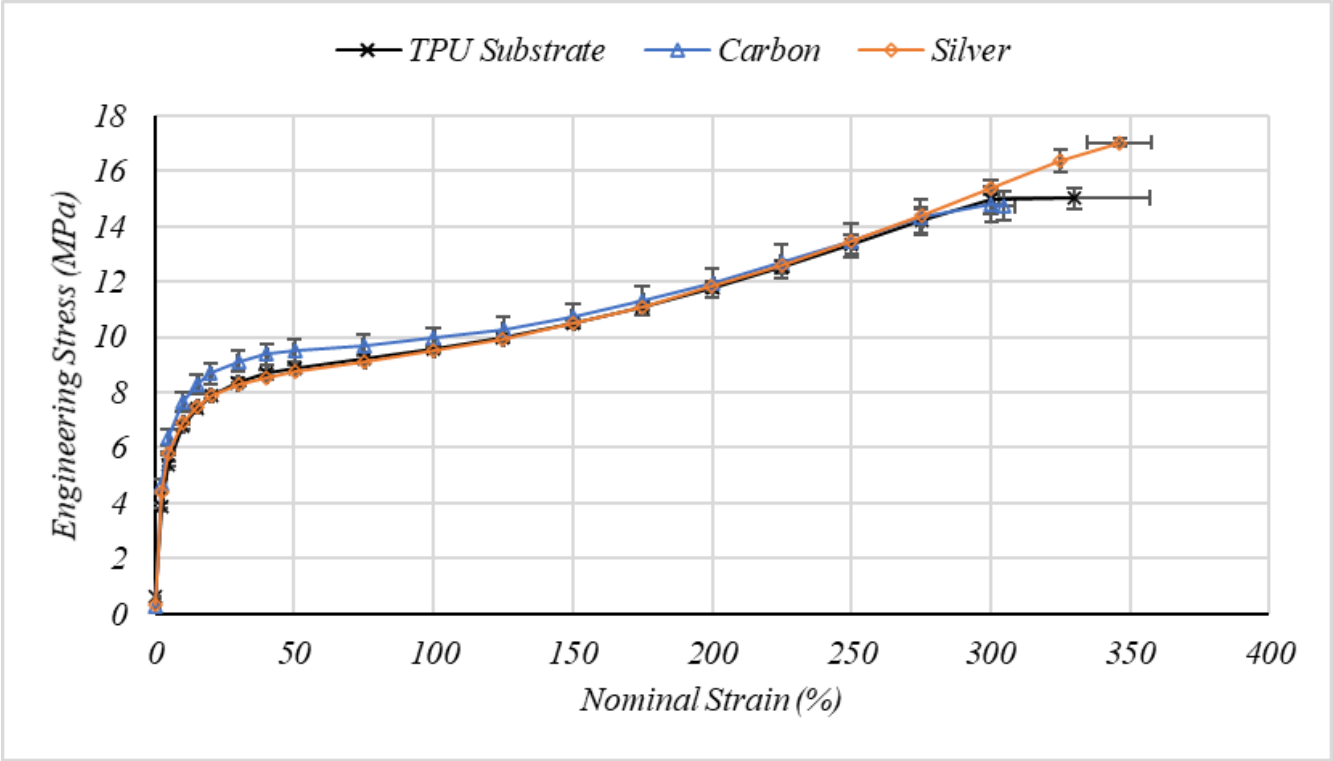
- Custom Hounsfield Tensile Testing Rig
- Simultaneous Logging:
  - Resistance
  - Stress/Strain
  - 150x5mm Samples
- 50mm/min extension rate
- Maximum Extension
- Cyclic Testing
  - 10% Nominal Strain





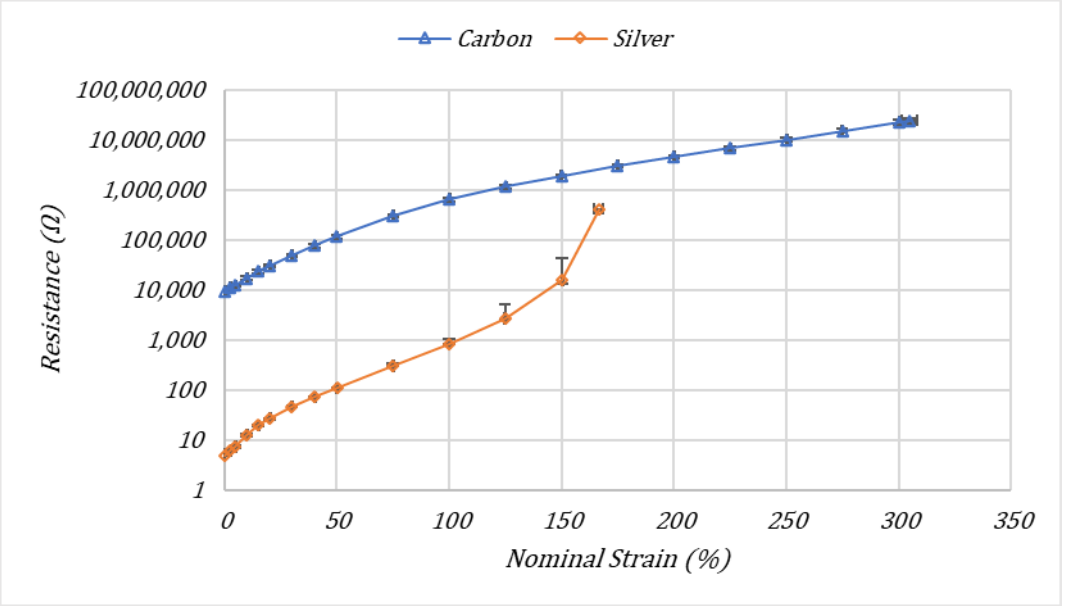
Stress Response

- Substrate dominate
  - Initial elastic deformation followed by plastic deforming to over 300% at break

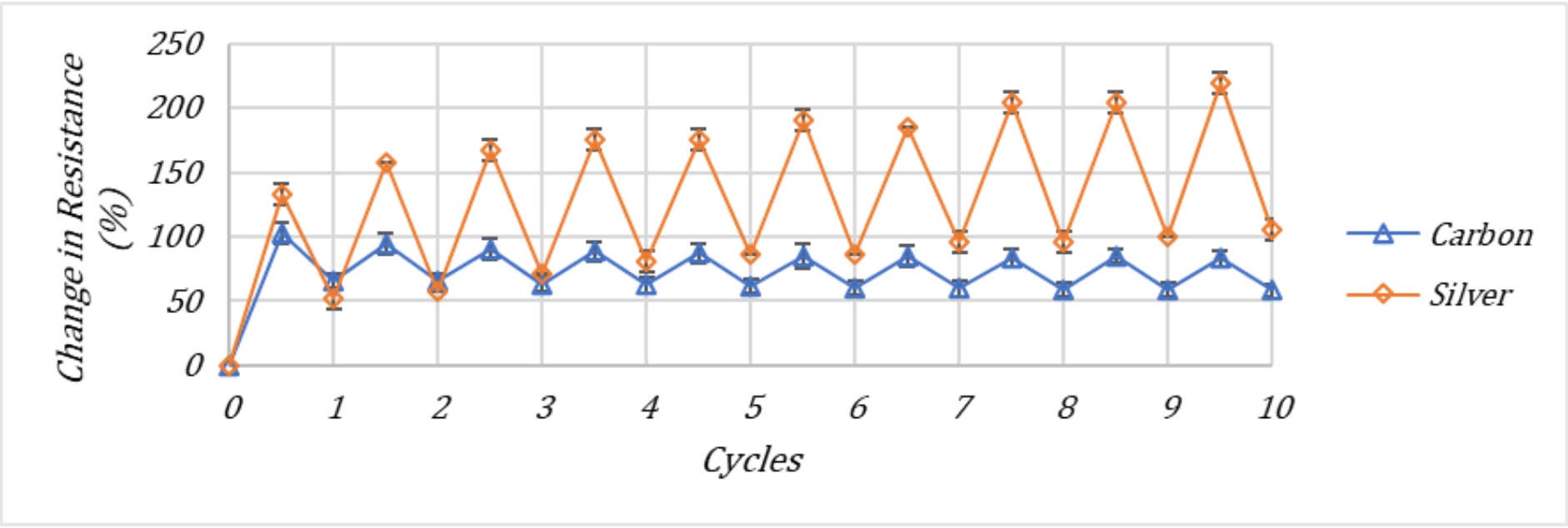


Maximum Extension

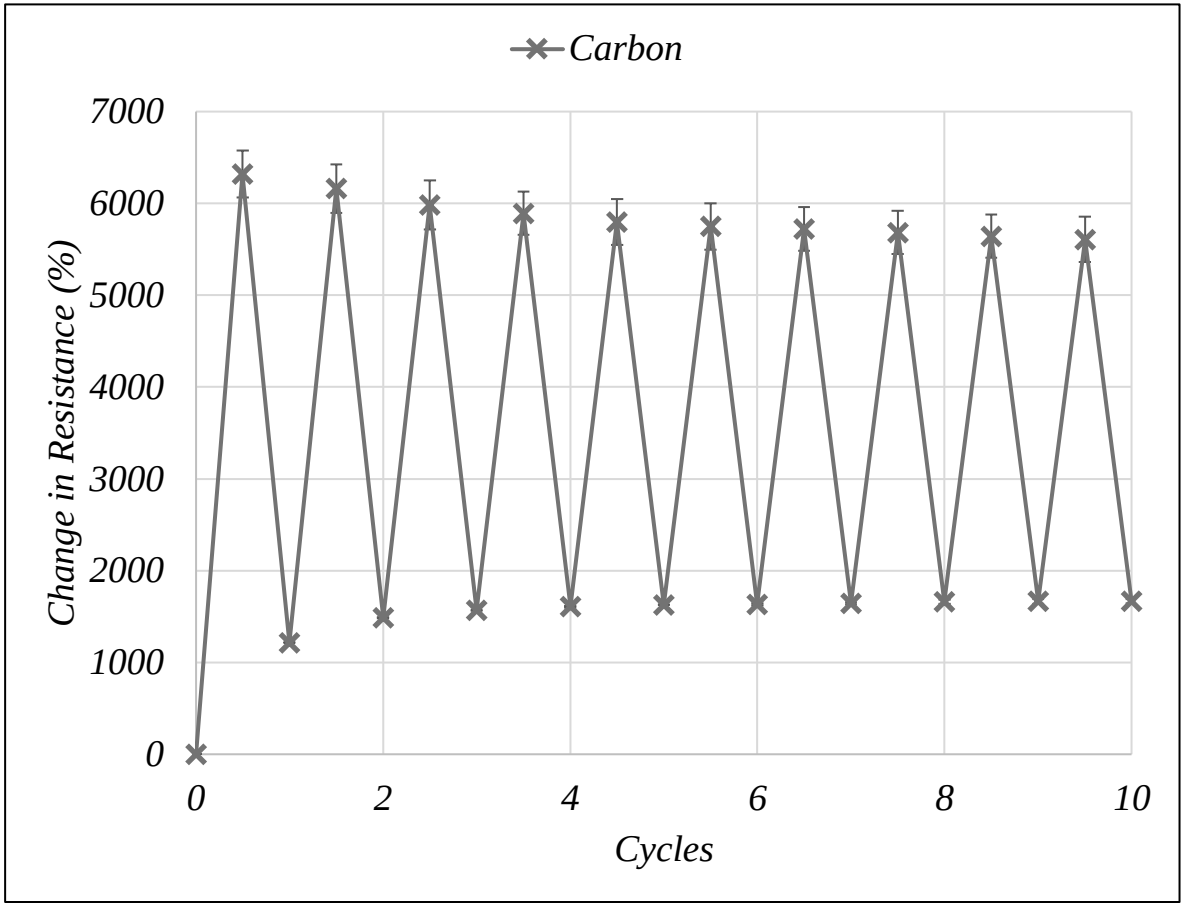
- Carbon
  - Conductive path maintained even as flakes pulled apart
  - Conductivity to 300% nominal strain
  - Low density/Higher surface area
- Silver
  - Distance between flakes increases with strain
  - Conductivity to 150%
  - Insulating resin
  - Network breaks
  - Percolation fails



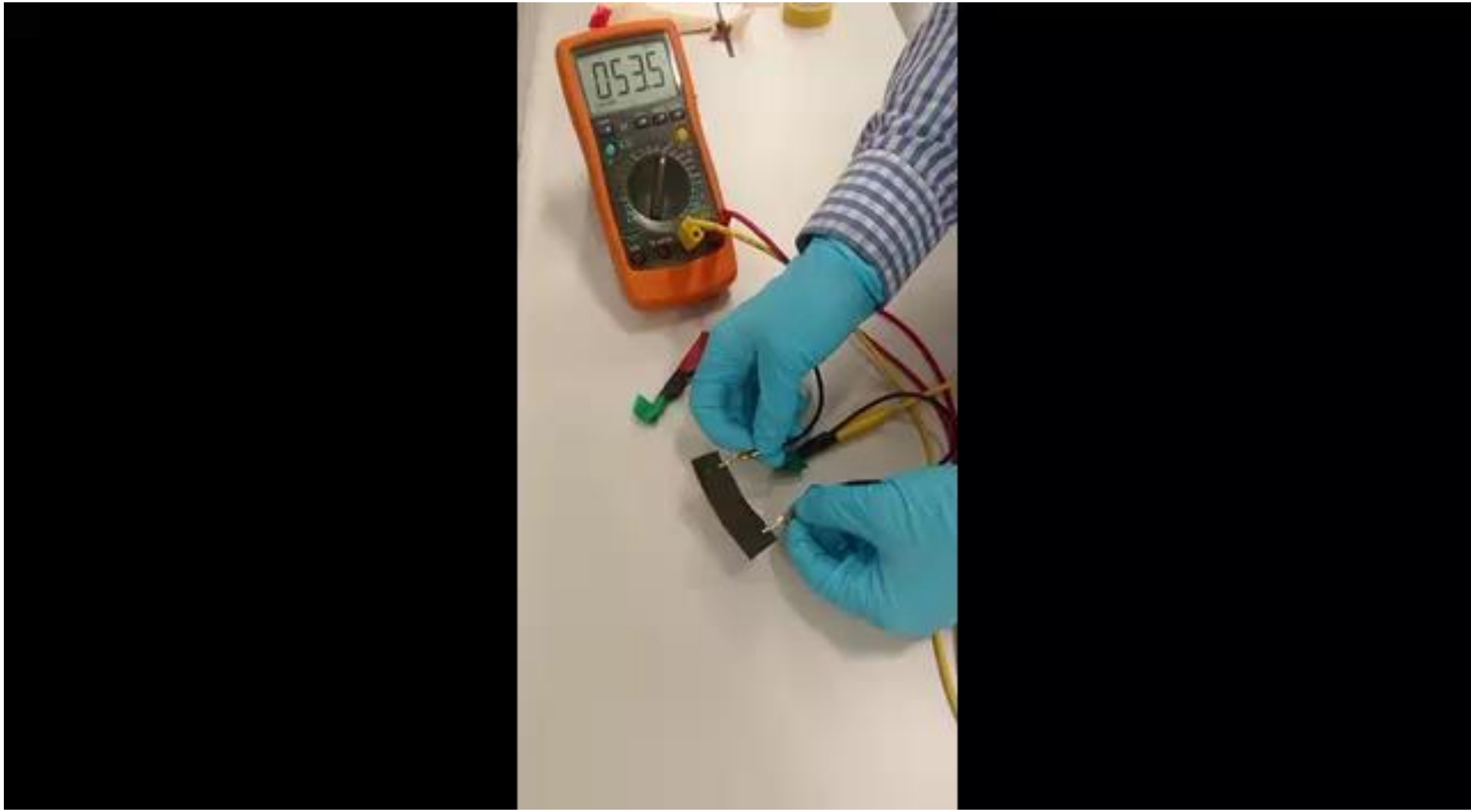
10% Cyclic Strain



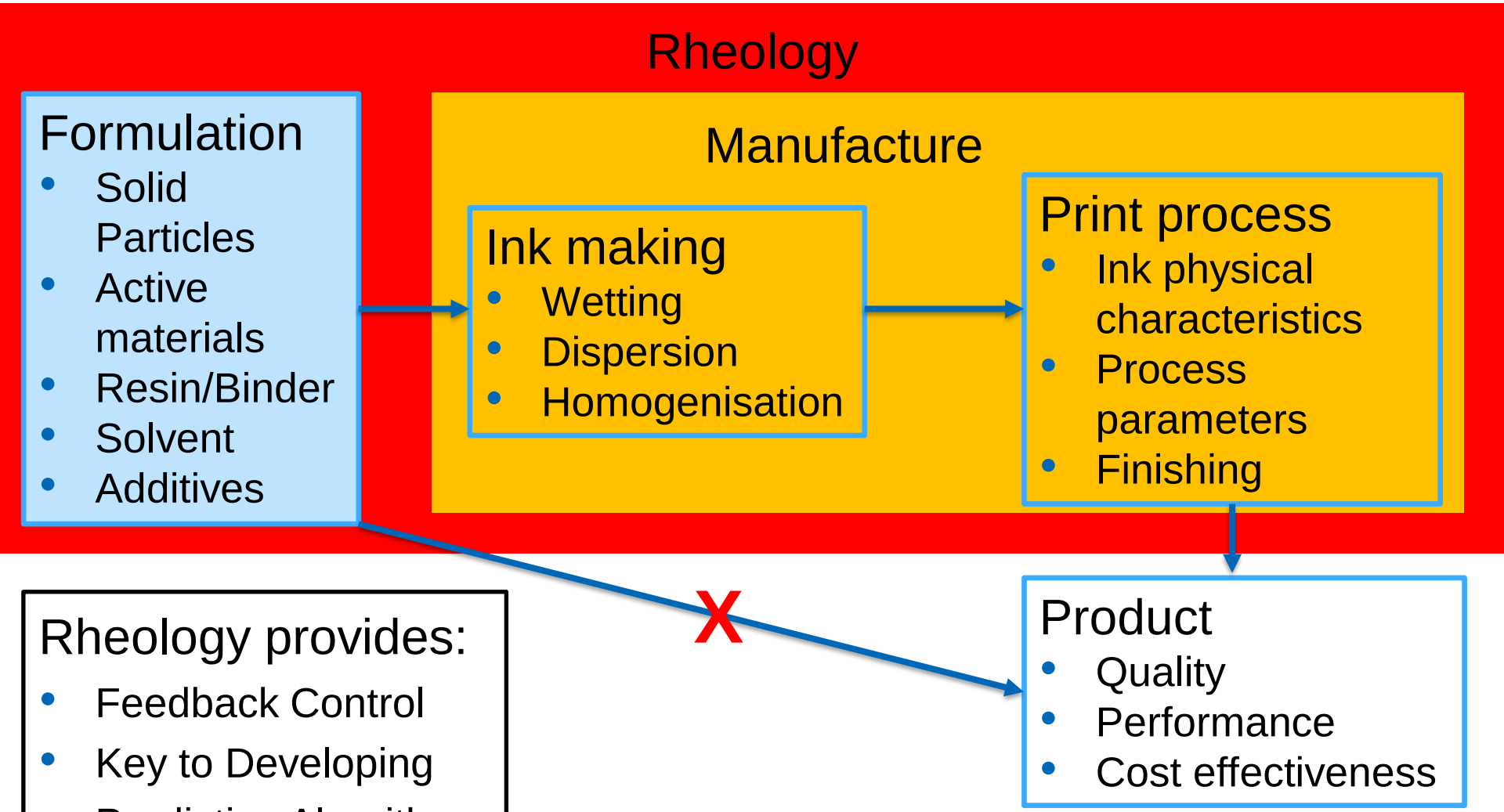
100% Nominal strain



Bend Test Video



Advanced Manufacture by Printing



Rheology provides:

- Feedback Control
- Key to Developing Predictive Algorithms

Why use Rheology?

- Printing is primary a fluid deposition technique
  - Understanding the fluid properties is critical to understand the process
  - Most inks and coating are non Newtonian with viscoelastic properties
- Quicker optimisation of formulations
  - approx. 2hrs for rheology testing compared to at least half a day for print trials
- Less materials required
  - Print trials use about 30ml of ink compared to 3ml for rheology
  - particularly important for some functional materials with high cost
    - Even cheap one such as Gold and Silver
- Less waste by improving quality control
  - Knowing how to correct batches which do not pass
- Improved print performance
  - Understanding how to make the ink match the process

What is viscosity?

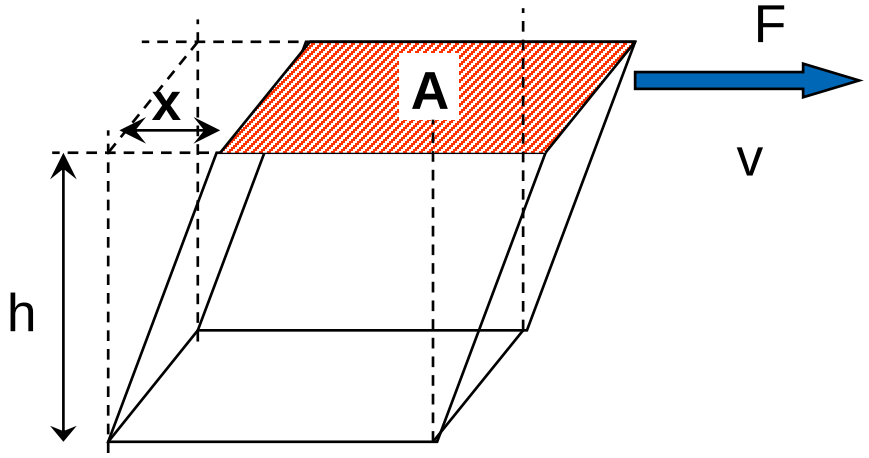
- How thick a fluid is
- Increased resistance to flow = increased viscosity

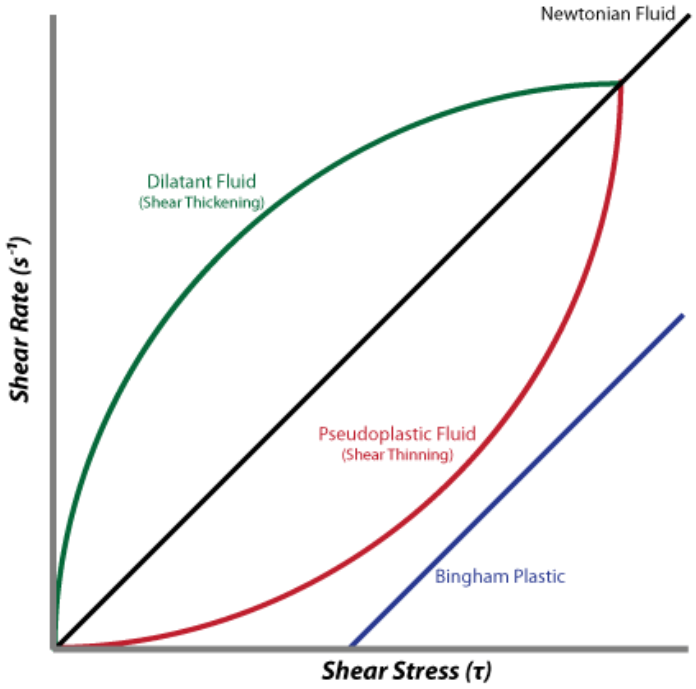
Increasing Viscosity

Viscosity

Viscosity – ratio of the shear stress to shear strain rate

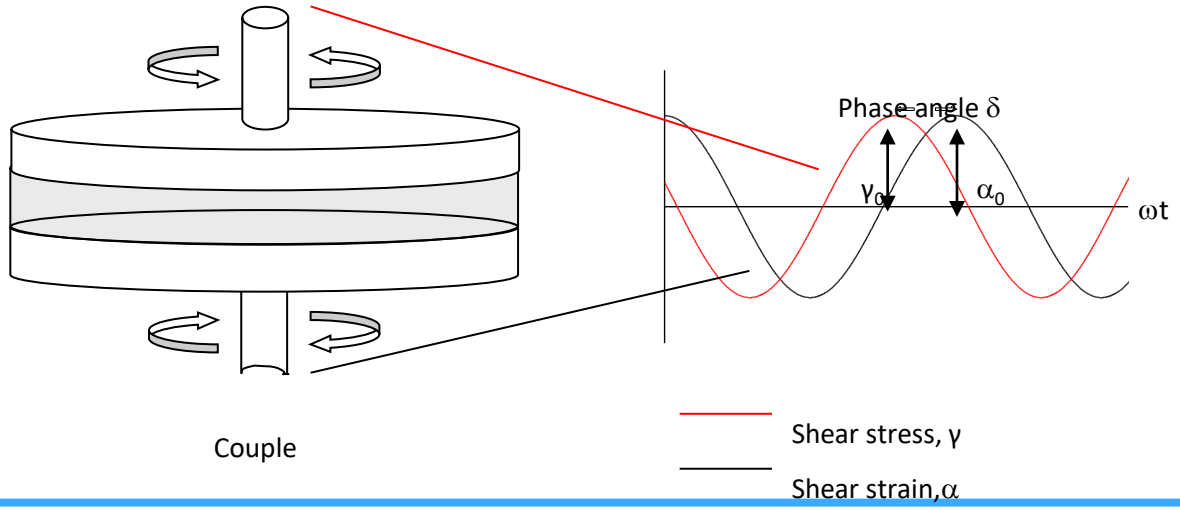
- Newtonian fluids – stress is directly proportional to the strain rate
  - Water, Silicone oil
- Non-Newtonian materials covers everything else
  - Printing inks





Oscillatory Rheology - SAOS

- Small amplitude oscillatory shear
- Produces the viscoelastic properties of the fluid
- By imposed stress, of known angular frequencies, which results in a harmonic strain response proportional to the stress amplitude, and with phase lag, relative to the stress, and which is independent of the applied stress amplitude



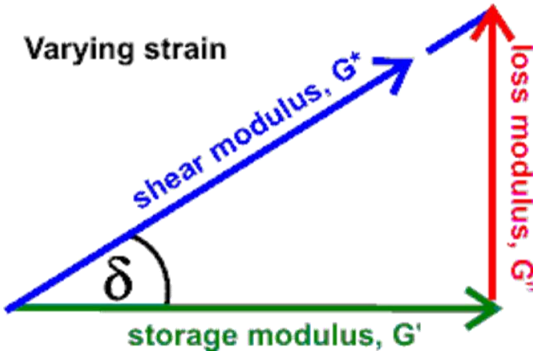
Viscoelastic Parameters

- By measuring the stress and strain associated with the sine waveform under SAOS a range of viscoelastic parameters can be determined
- These include:
  - G* - Complex Modulus
  - δ - Phase Angle
  - G' – storage modulus
    - magnitude of the elastic component of a material and is a measure of the energy stored
  - G'' – Loss modulus
    - magnitude of the viscous component of a material and is a measure of the energy dissipated per cycle of sinusoidal deformation

$$G^* = G' + iG''$$

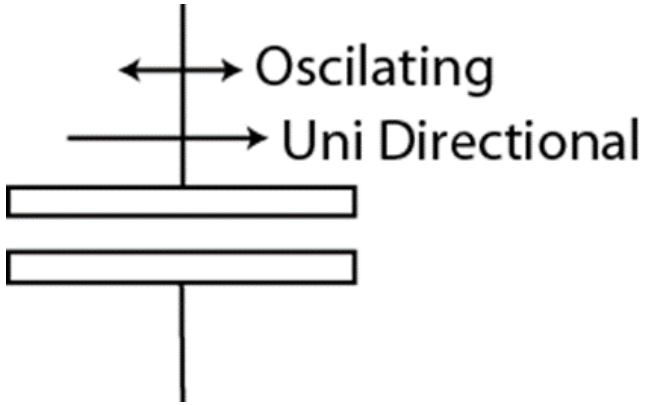
$$G' = \frac{\sigma_0}{\gamma_0}\cos(\delta)$$

$$G'' = \frac{\sigma_0}{\gamma_0}\sin(\delta)$$

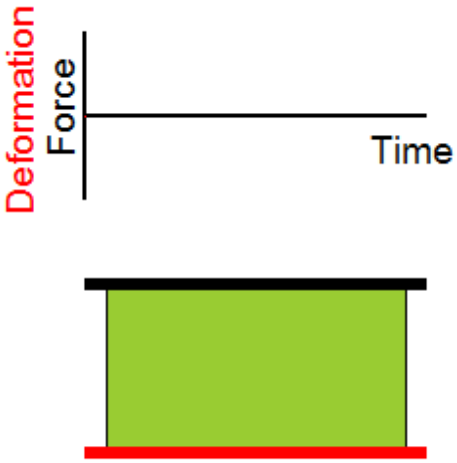


Controlled Stress Parallel Superposition (CSPS)

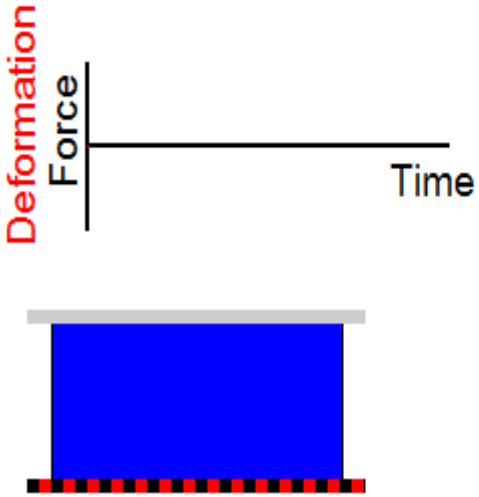
- Application of a continuous unidirectional flow on top of a SAOS measurement
- Linearity of the SAOS measurement must be obtained under flow using the same method as described earlier
- Allows for the viscoelastic properties of the fluid to be determined under flow conditions
- Improved correlation between rheology and print performance



SAOS (Quiescent)



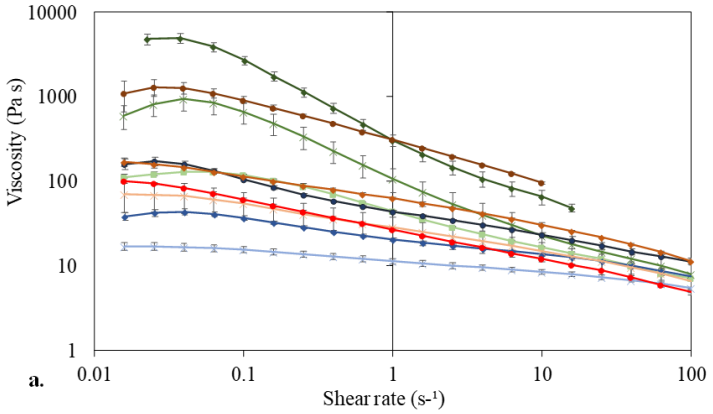
CSPS (Flow Conditions)

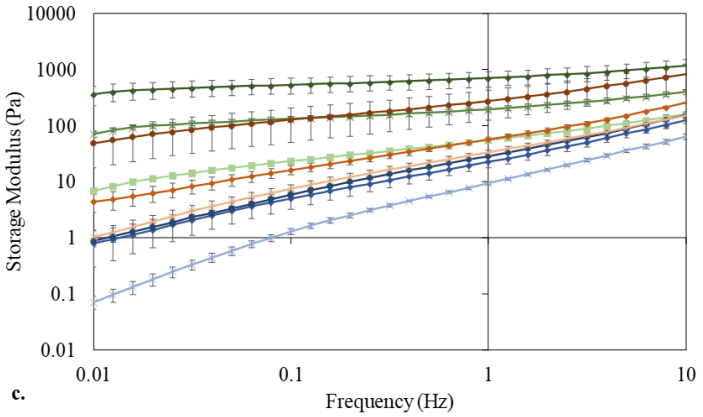


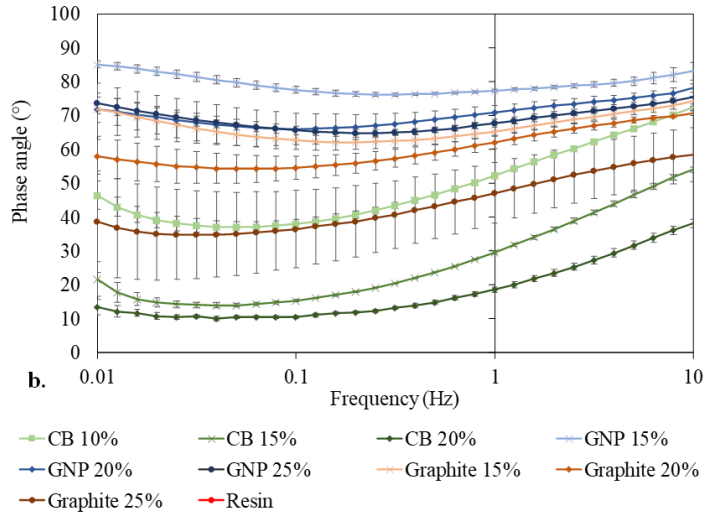
G’	Storage Modulus
G’	Loss Modulus
δ	Balance of Loss and Storage moduli

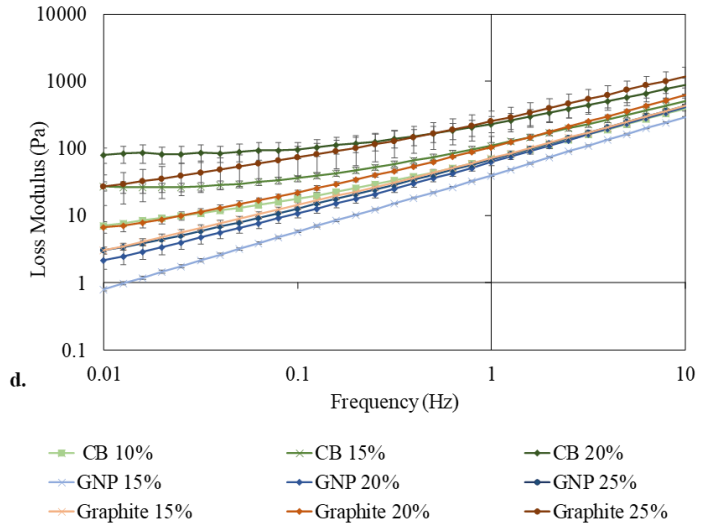
$G'_{\|\|}$	Storage Modulus under CSPS
$G''_{\|\|}$	Loss Modulus under CSPS
$\delta_{\|\|}$	Balance of Loss and Storage moduli under CSPS

Impact of different shape particles





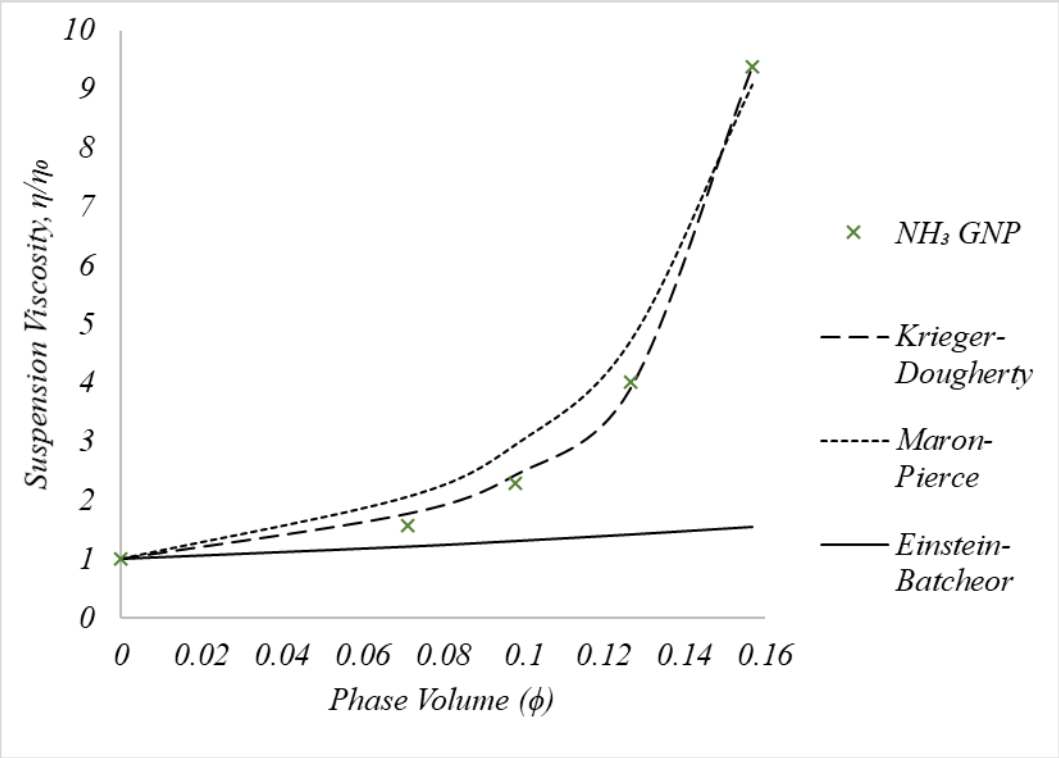




- Carbon black – Spheres – Mean particle size 50 nm
- GNPs – Flakes – Typical planar size 0.3-5 µm
- Graphite – Flakes – Typical D90 17.9 µm

P²CAR – Flagship project 2018
EPSRC Centre for Innovative Manufacture

Predicting the viscosity of suspensions of irregularly shaped particles



Effect of particles on viscosity

Models fitted to experiments

Best fit with Krieger Dougherty equation

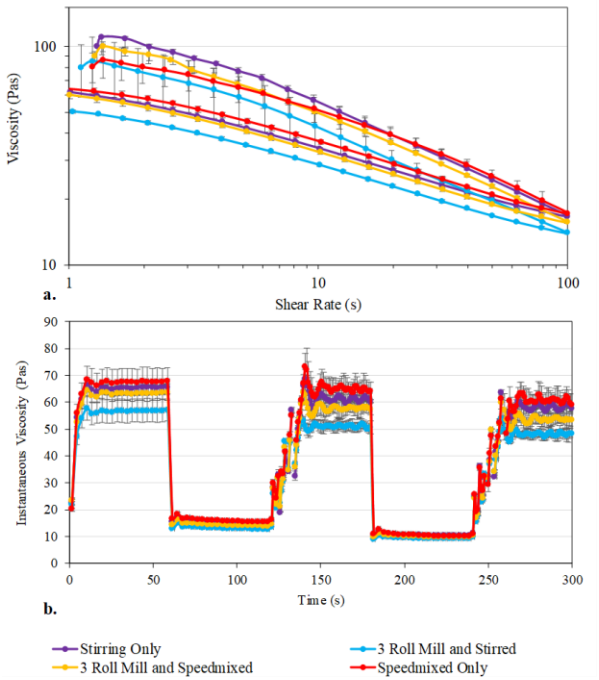
Information on particles:

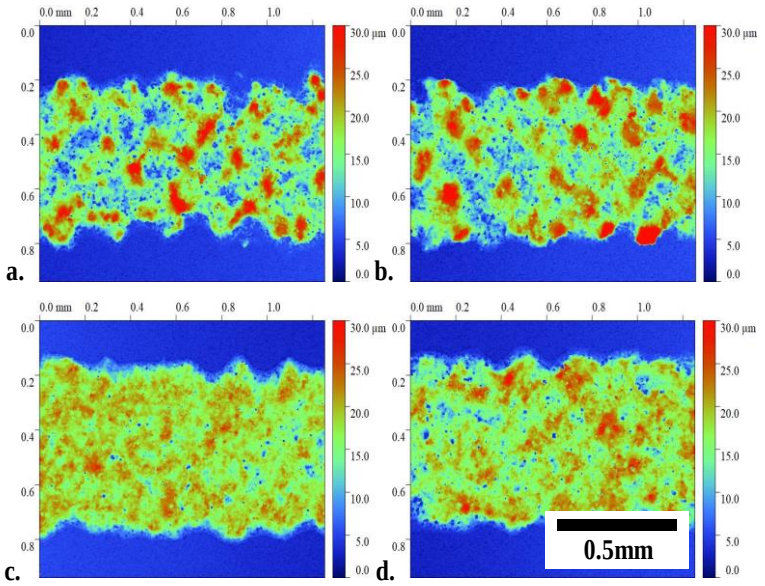
- Size and shape
- Maximum packing fraction
- Intrinsic viscosity
- Dispersion

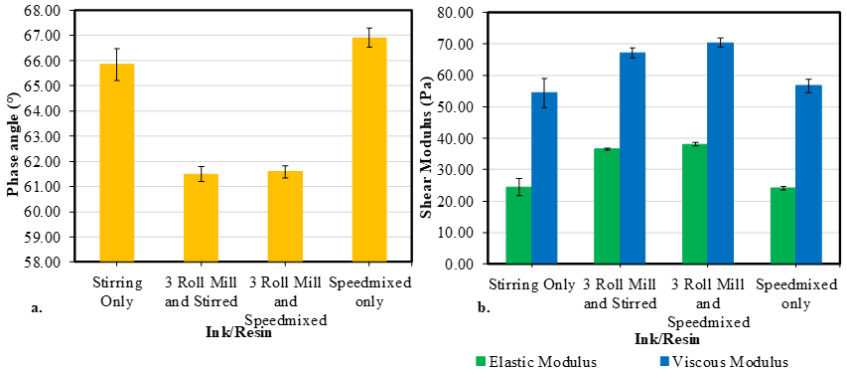
Guide future ink formulation

Ref: "Rheology of high-aspect-ratio nanocarbons dispersed in a low-viscosity fluid" Journal of Coatings Technology and Research – DOI: 10.1007/s11998-020-00319-2

Influence of Manufacture





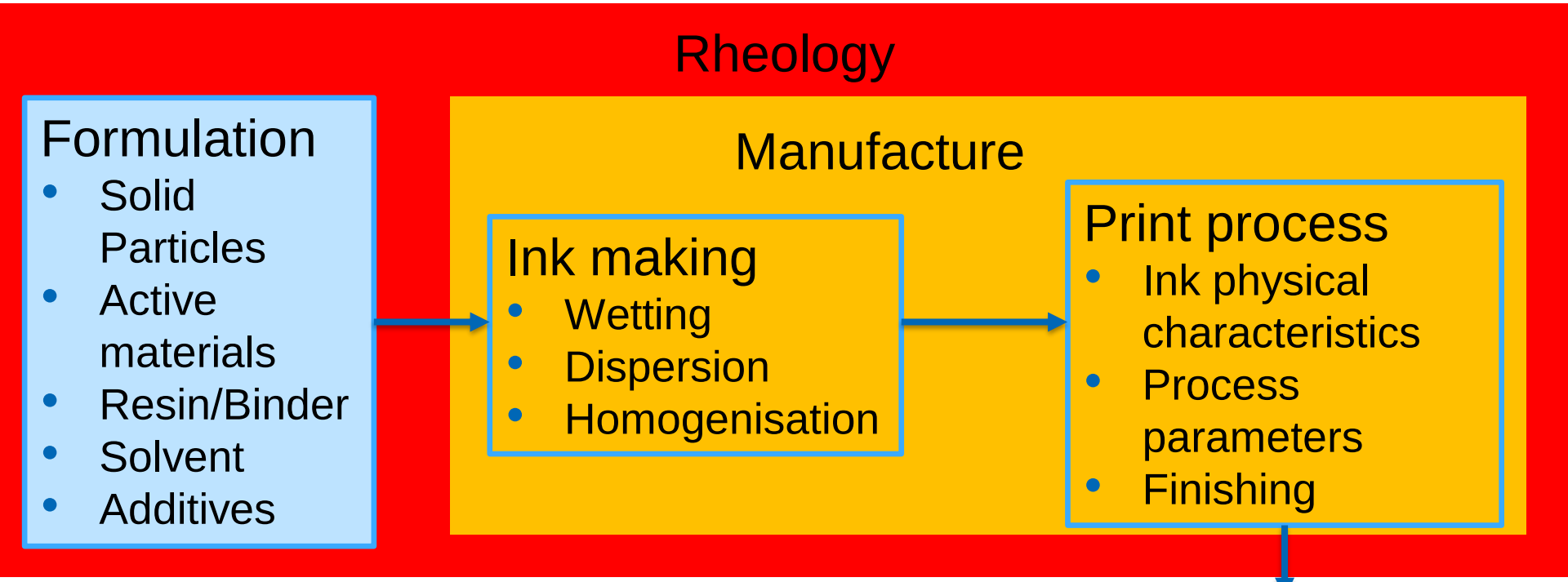


Ink Manufacturing processes

- Wetting – displace air from around the pigments
- Dispersion – 3 roll mill, bead mill
- Homogenisation – stirring, speed mix

Ref: EngD "Advanced Manufacture by Screen Printing"
Sarah-Jane Potts, Swansea University 2020

Advanced Manufacture by Printing



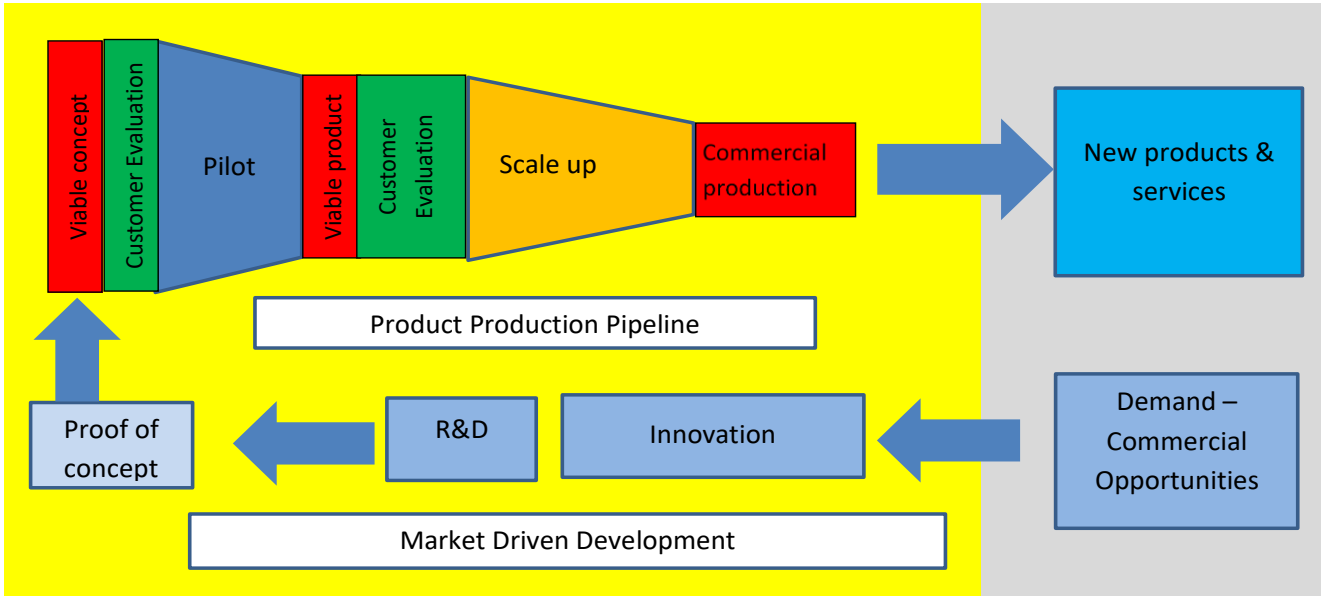
Rheology provides:

- Feedback Control
- Key to Developing Predictive Algorithms

Product

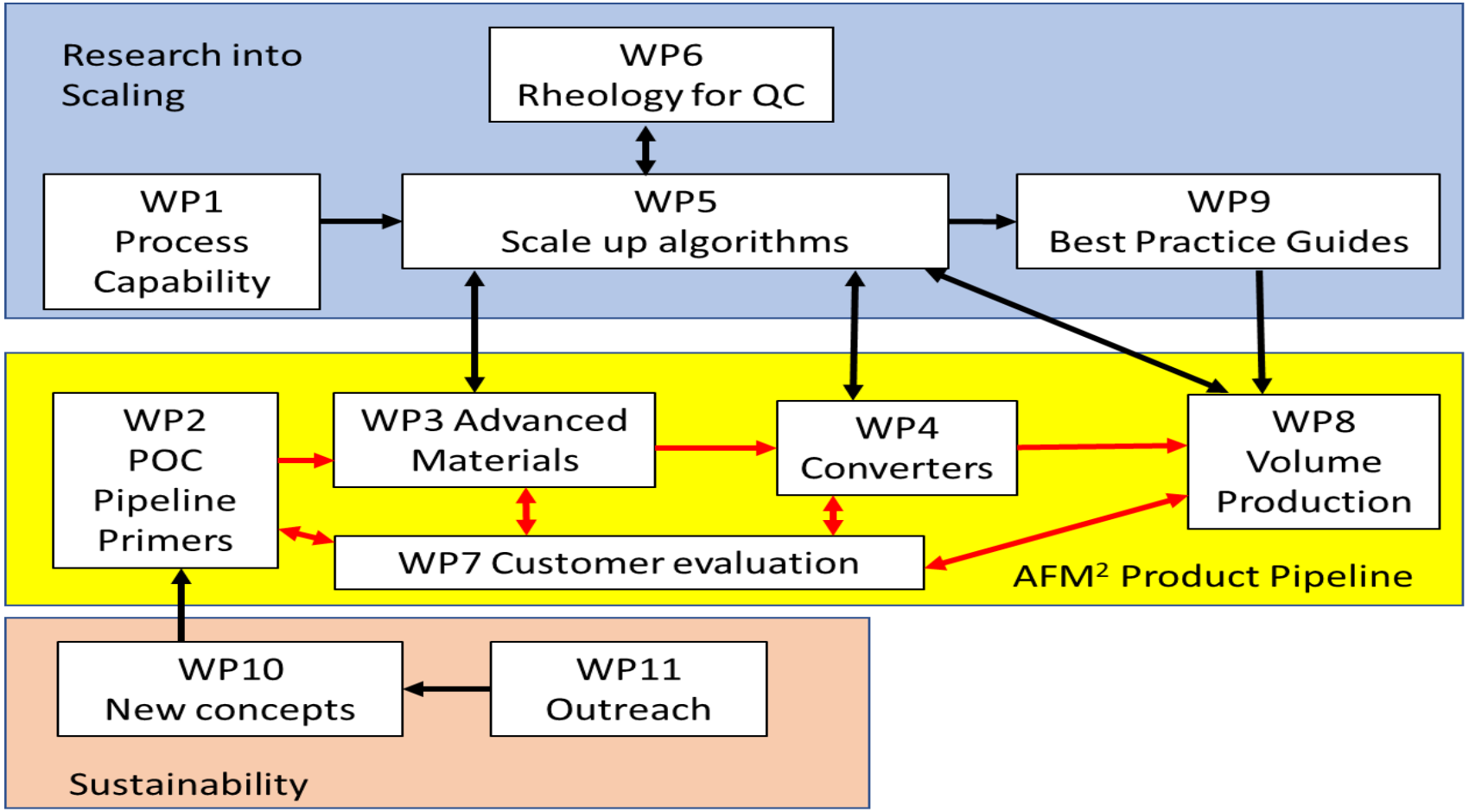
- Quality
- Performance
- Cost effectiveness

Turning demand into products by advanced manufacture by printing



- Identifying Demand – commercial opportunities for new products and services
- Innovation – identifying potential solutions
- Proof of concept – turning solutions into a bench prototype
- Concept evaluation – accessed by potential users
- Pilot production – for market and customer evaluation
- Customer Evaluation
- Scale up to volume production – efficient, quality products in reasonable quantities

Application of Functionalised Micro & Nano Materials – scale up to volume production



A multidiscipline approach covering the whole supply chain

Closure

- Flexible and stretchable ink for wearable applications
  - Carbon ink
    - Conductive to 300% nominal strain
    - Cyclic strain
  - Silver ink
    - Conductive to 150% nominal strain
    - Resistance increase with number cycles
- Inks are a complex blend of solid particles, resins and solvents
  - Elastic resin dictates flexibility
  - Performance Trade off between increasing particle loading and flexibility/printability
  - Surface area is key
- Rheology is key to:
  - Understanding the relationship between formulation and printability
  - Process control and Quality Assurance
- Advance Manufacture by Printing Pipeline – innovative concepts to volume production

Acknowledgements

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  - David Gethin – WCPC founder and director
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Welsh Centre for Printing and Coating (WCPC)

Summer School “Printing for Functional Applications”, 2021