# Production and Applications of Microfibrillated Cellulose and Mineral/ Microfibrillated Cellulose Composite Materials

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# The Products: Microfibrillated cellulose (MFC) and Mineral/ MFC composites

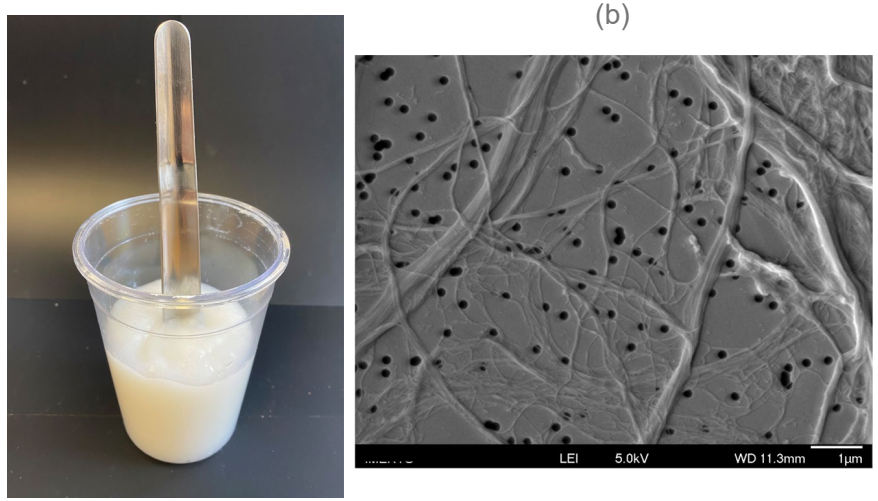
- Two products:
- (i) MFC
- (ii) Mineral MFC Composites

- Viscous suspensions with fibril solids ~1-2 %

(i): MFC

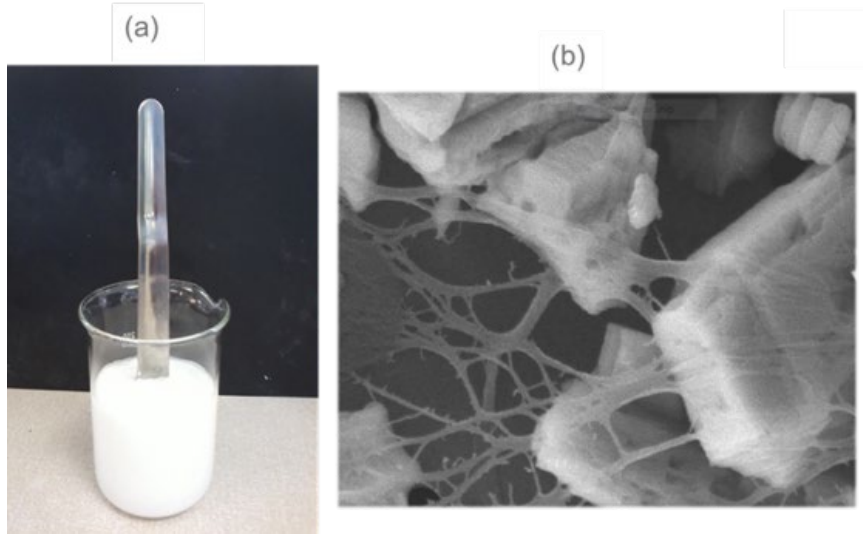
(a)

(b)




*Photograph (a) and micrograph (b) of MFC showing the high viscosity and fibrillar structure*

(ii): Mineral MFC Composites




*Photograph (a) and micrograph (b) of mineral/ MFC composite showing the high viscosity and fibrillar structure*

# The Production Process 1: Mechanical fibrillation of cellulose pulp in a wet grinding process

- Processing and handling of MFC is dominated by the high viscosity of MFC arising from presence of high surface area hydrophilic fibrils
- Cost effective grinding-based method to produce MFC and mineral/ MFC composites
- In some cases, cellulose fibres are co-processed with mineral particles.  The mineral particles act as micro-grinding media, thus, reducing the energy requirement
- Process accomplished using robust, industrially proven grinding equipment
- Scalable
- Proven at full-scale

# Fibre raw materials

**Fibre sources**

- Wood-free v mechanical
- Kraft v sulphite
- Long fibre v short fibre
- Virgin v recycle
- Tree-based v other biomass
- ....

**Properties**

**Engineered fibrils**

- Fibril length
- Fibril width
- Microgel-like or discrete
- Surface charge
- Surface hydrophobicity
- Colour
- ……

- **Performance**
- Enhancement of web properties (mechanical, porosity, surface, optical)
- Viscosification/ rheological property modification
- Reinforcement
- Stand-alone objects
- Barrier
- Cost-effectiveness
- Re-use
- ……..

# Minerals

**Mineral sources**

- Calcium Carbonate
  - Ground marble/ limestone
  - Ground chalk
  - Precipitated
- Kaolin
  - Hydrous
  - Calcine
  - Halloysite
- Andalusite
- Ball Clay
- Bauxite
- Bentonite
- Clinoptilolite
- Diatomite

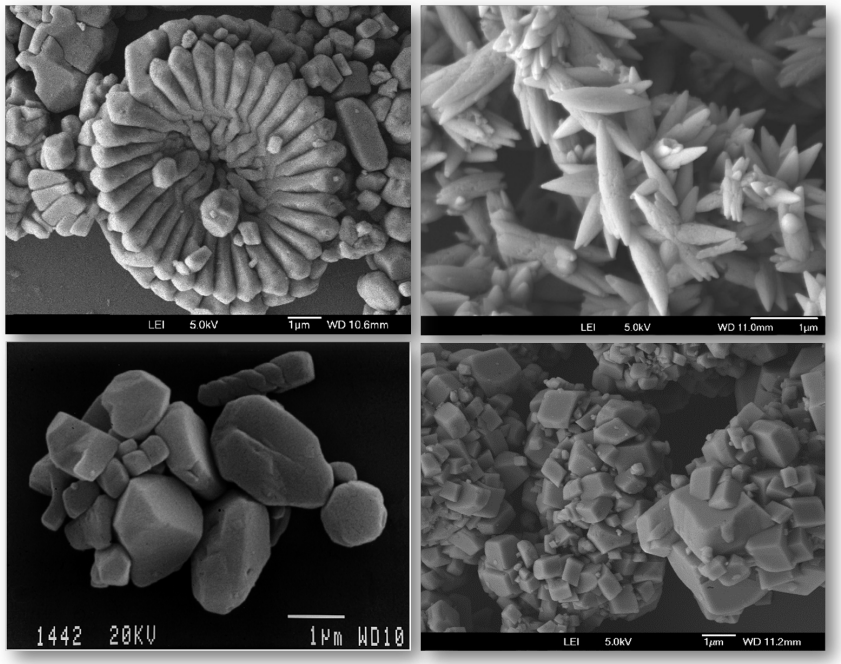
- Dolomite
- Expandable Graphite
- Feldspar
- Fused Alumina
- Fullerenes
- Fused Silica
- Mica
- Natural Graphite
- Perlite
- Specialty Carbon Black
- Synthetic Graphite
- Vermiculite
- Zirconia

**Properties**

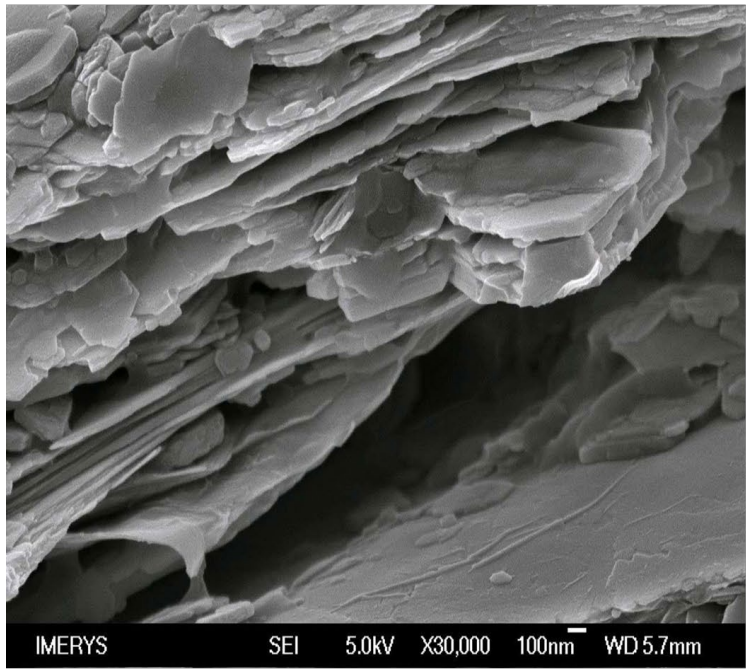
- Particle size
- Particle shape
- Particle packing
- Crystal microstructure
- Colour
- Reflectance
- Absorbance
- Scattering efficiency
- Refractive index
- Specific gravity
- Hardness
- Chemical composition
- Surface character
- ….

- **Performance**
- Opacity
- Clarity
- Gloss
- Density modification
- Wear / abrasion resistance
- Barrier
- Blocking
- Flame retardant
- Mechanical reinforcing
- Chemical delivery/ reaction
- ……

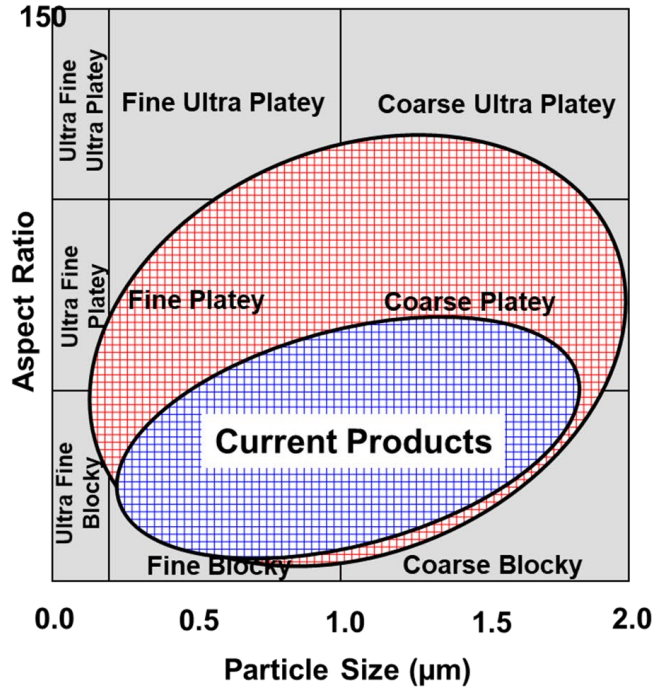
# Minerals




Calcium carbonate: Ground and precipitated forms: High level of control over crystal morphs and dimensions

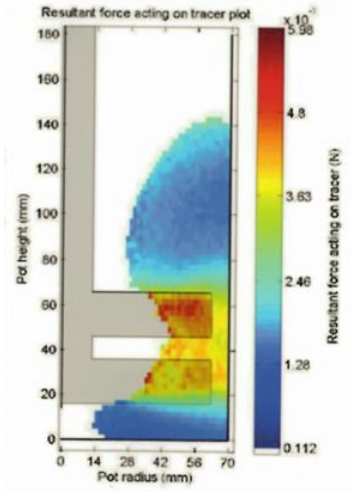



Kaolin: Can be engineered for very high shape factor



# Recent learnings 1

- How to produce high quality MFC from  a wide range of virgin and recycle feeds
- How to produce MFC without using minerals where required
- Key is optimisation of grinding environment for each feed material




Supermill programme,

Engineering and Physical Sciences Research Council

Formulations Centre for Doctoral Training

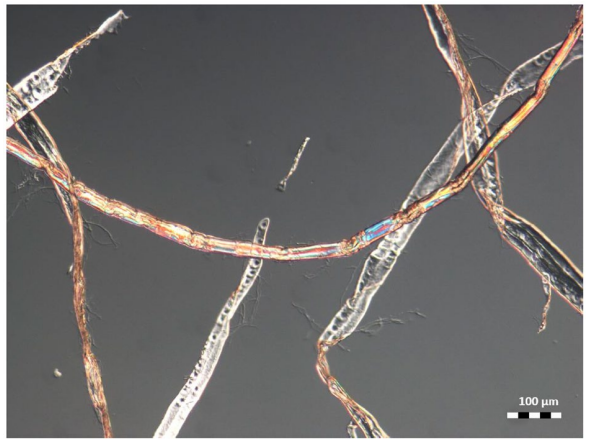
University of Birmingham UK

PEPT* mapping of grinding environment,

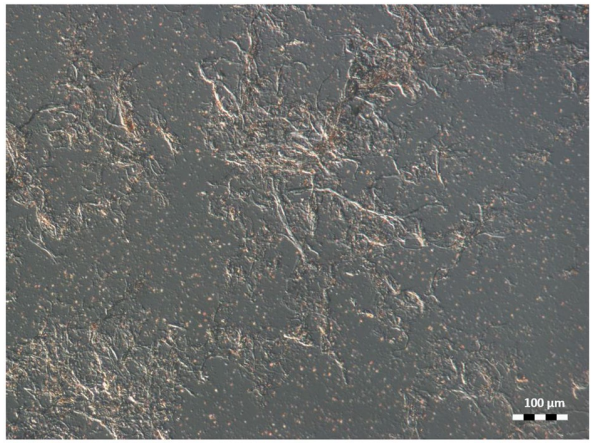
Rowson Group, University of Birmingham

*Positron Emission Particle Tracking

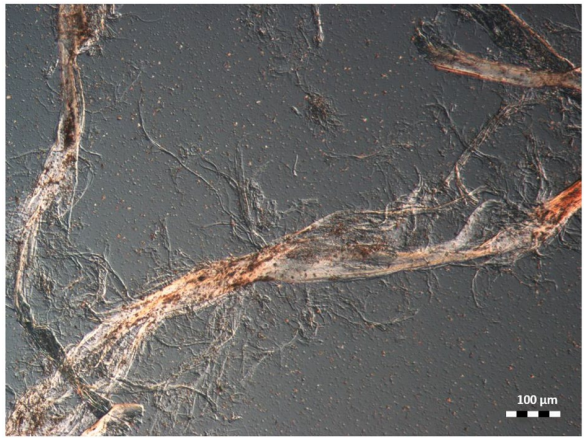
# Recent learnings 2



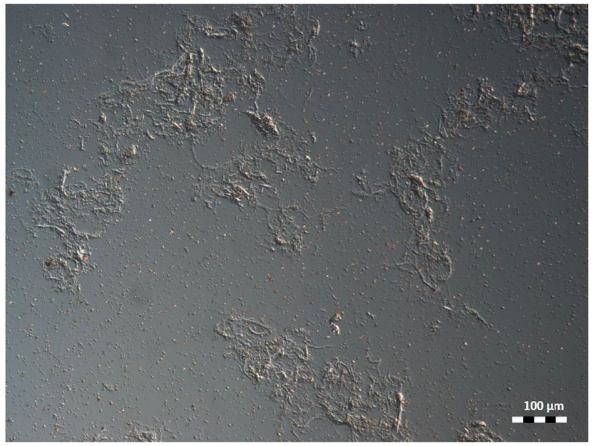

Unprocessed



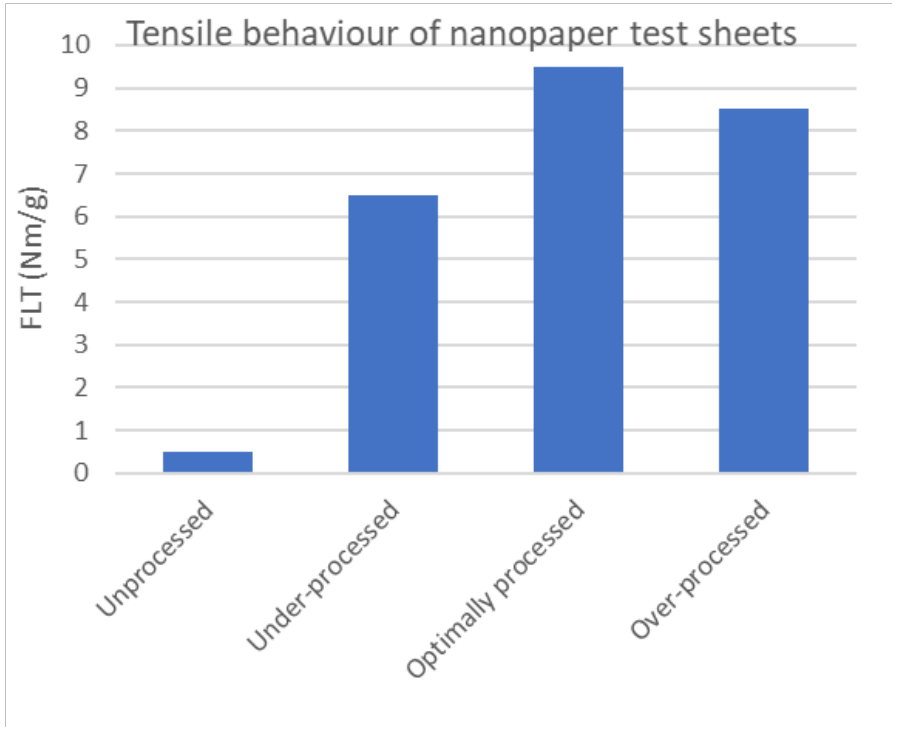

Optimally processed




Under processed

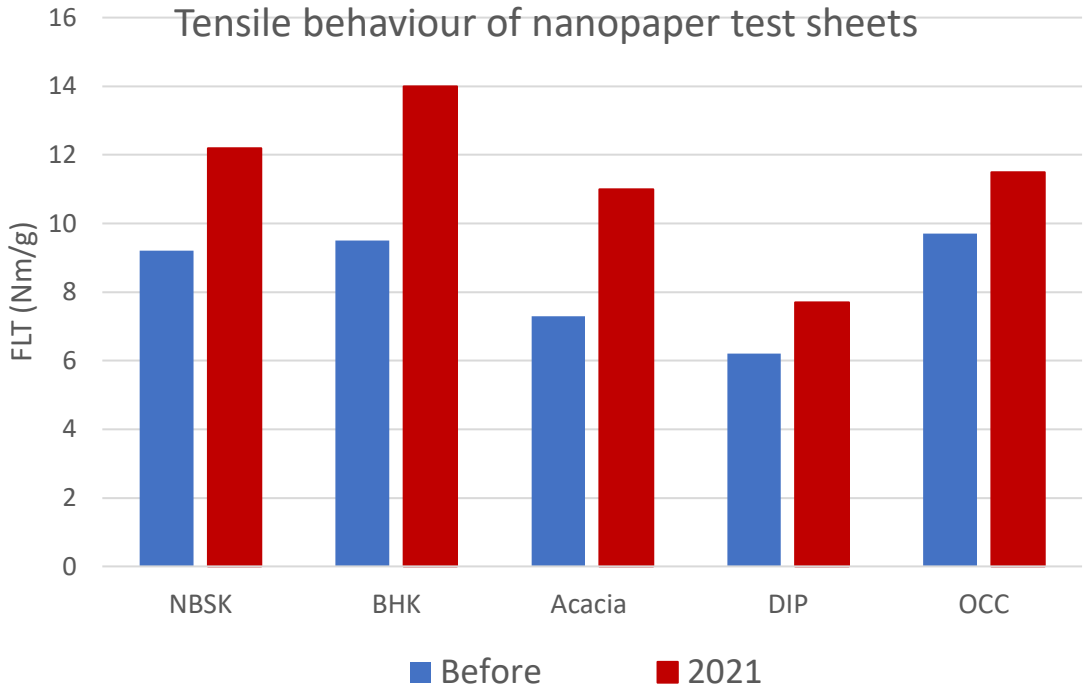



Over processed




Process can be optimised for different feeds

# Recent learnings 3




- Process optimisation has allowed preparation of MFC samples with increased tensile properties

# Applications - Increased bonding in fibre-based structures: Paper and Board 1

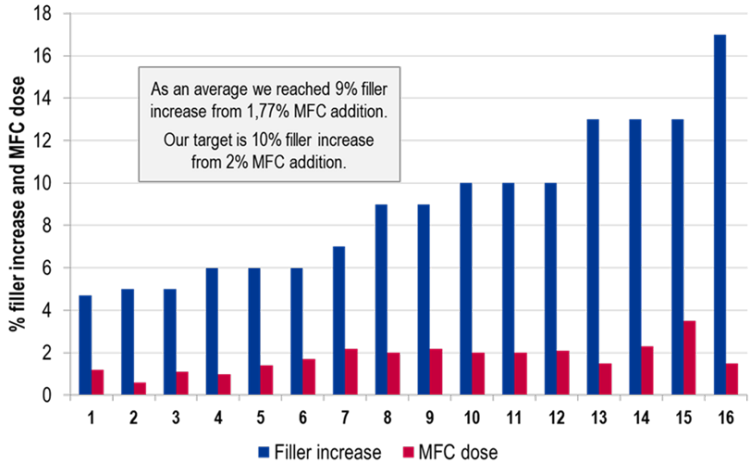
- Use of filler in paper and board allows:
  - Improved optics
  - Improved printing
  - Generally degraded mechanical properties
  - Reduced cost
- Use of MFC in paper and board allows:
  - Generally improved mechanical properties
  - Lower porosity and hence improved coating hold out
- Use of MFC and filler together can allow preparation of papers and boards with new balances of properties and costs

- Many applications, including:
  - Wood free printing and writing paper
  - White top liner packaging
  - Newsprint and magazine papers
  - Barriers
  - New product development opportunities

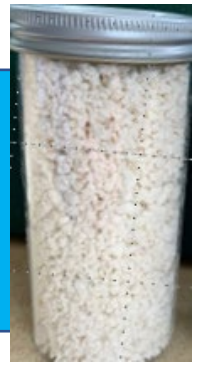
# Applications - Increased bonding in fibre-based structures: Paper and Board 2

## Wood free printing and writing papers

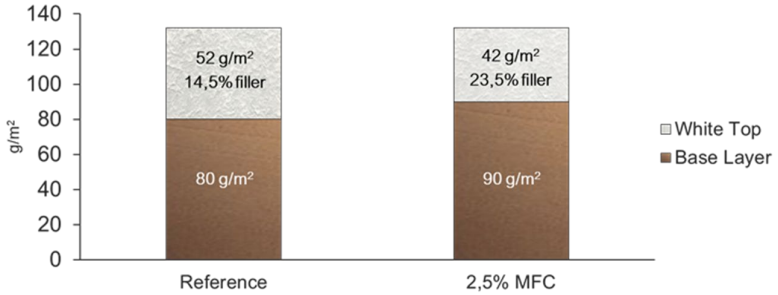
16 full scale paper machine trials




Mineral/ MFC composite
- GCC, PCC, kaolin
- NBSK, BSK, BHK, UBHK, sulphite
- Virgin fibres



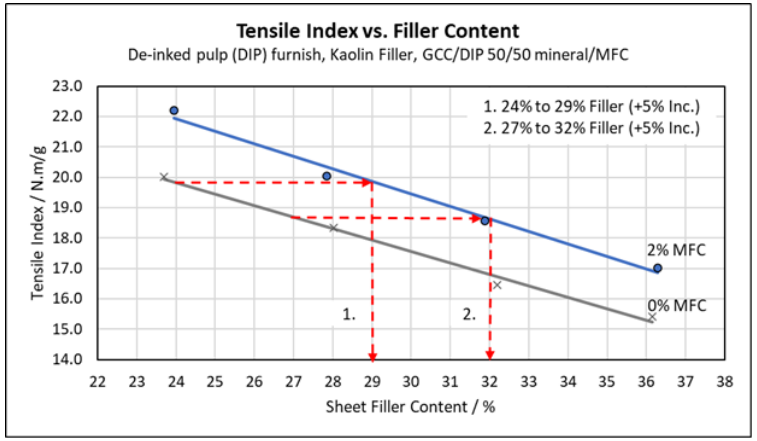
## White top liner




- MFC addition to the top layer improves strength, enabling the filler content to be increased.
- Increased filler content improves the optical coverage of the dark base, enabling the top layer thickness to be reduced.
- The base layer can then be increased proportionately to maintain/improve overall WTL properties.
- This substitution of white top fibre reduces overall costs whilst maintaining critical properties.

Mineral/ MFC composite
- GCC
- Office waste

## Newsprint and magazine papers

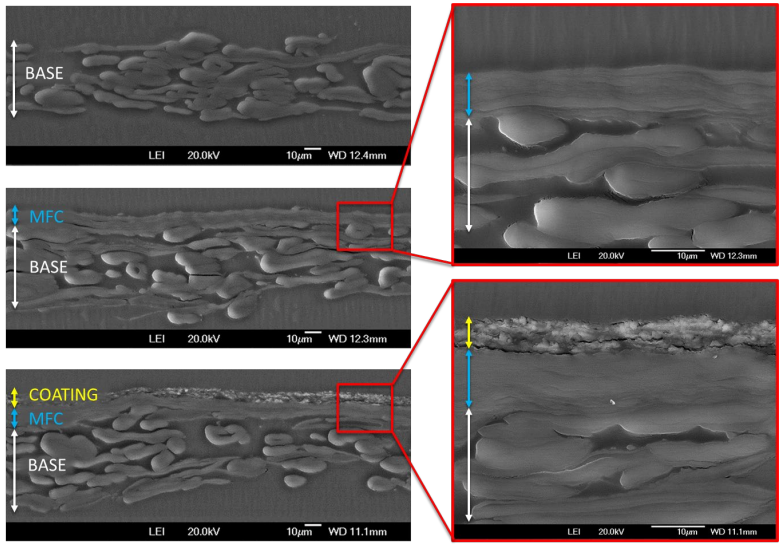



- Use of MFC based on DIP fibre enables sheet strength to be maintained when increasing the filler content, reducing overall costs.

Mineral/ MFC composite
- GCC
- DIP

# Applications - Increased bonding in fibre-based structures: Paper and Board 3

## Barriers applications

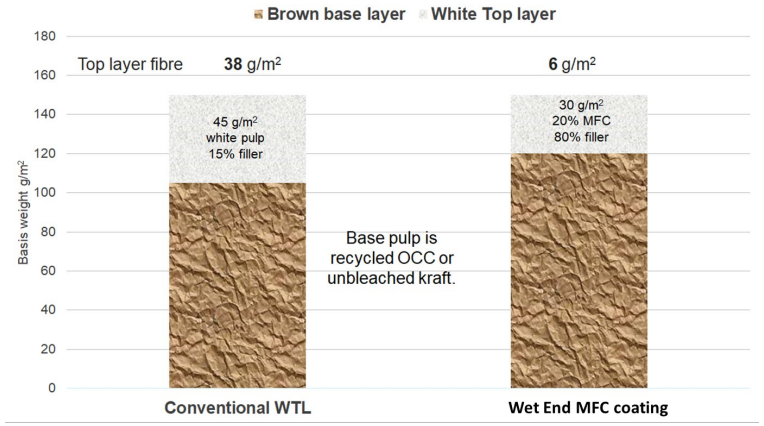


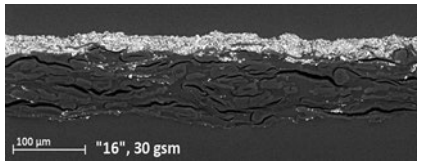

Cross-section Imaging: Scanning Electron Microscopy (SEM)

- Barrier properties of MFC: Oil & Grease, Oxygen, Aromas, Mineral Oils.
- Very smooth and closed surface for combining with additional functional coatings (e.g., To achieve water/moisture barrier).

**MFC**
- No minerals
- BSK, BHK, UBHK
- Virgin and recycle fibres

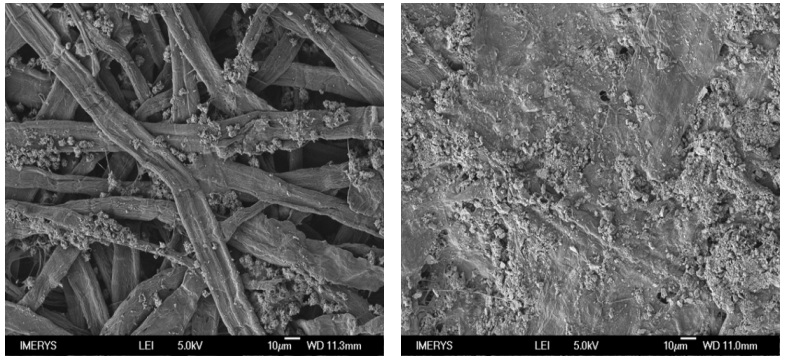
## New product development directions: Wet end coating




**Mineral/ MFC composite**
- GCC (high loading)
- Virgin and recycle fibres

## New product development directions: Very high filler loadings

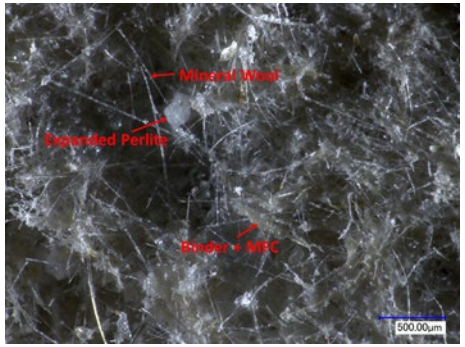



Scanning electron micrographs of uncoated wood free sheets; 17% GCC filled sheet with no MFC (left, control) and 55% GCC filled sheet with 4.5% MFC fibrils (right)

**Mineral/ MFC composite**
- GCC (80%))
- Virgin NBSK

# Applications - Increased bonding in fibre-based structures: Tiles and Boards

## Ceiling tiles



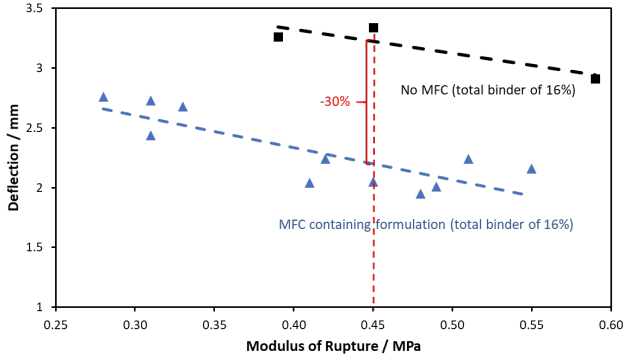




Image (upper left) and optical micrograph (upper right) of ceiling tile containing 8% MFC, with density of 160 kg·m$^{-3}$ and 300 x 300 x 18 mm in dimension.
sag resistance is measured as deflection of tiles at 90 %RH, 38°C for 24 h. The data of sag resistance vs. MOR demonstrate the use of MFC to improve sag resistance and strength. The acoustic performance is unaffected

Mineral/ MFC composite
- GCC
- Virgin and recycle fibres

## Construction boards

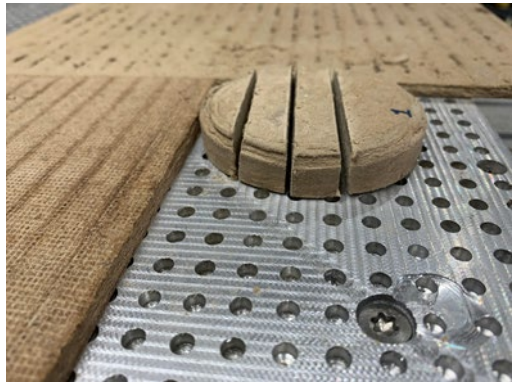
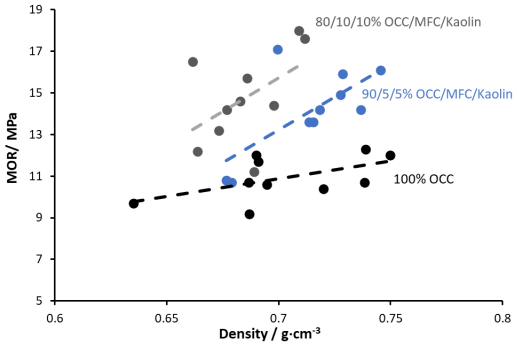


Image of fibreboards containing 5% MFC, with density of 700 kg·m$^{-3}$. The fibreboards are either round discs (7 cm in diameter, 6 mm in thickness) or large boards (300 x 300 x 6 mm in dimension), made from filtration, cold press and hot press



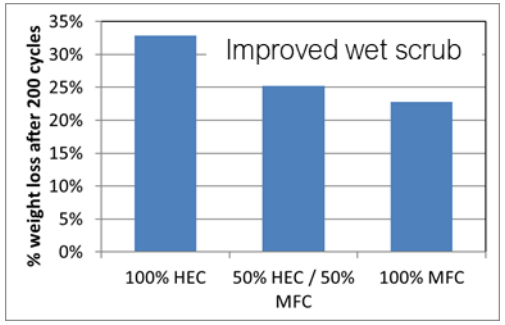

Effect of board density on strength. The addition of MFC improved the bending strength of the board.

Mineral/ MFC composite
- GCC and kaolin
- OCC

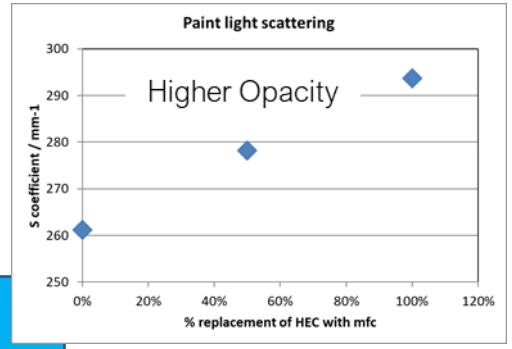
# Applications - Viscosification

## Paints and coatings

Substituting HEC with MFC

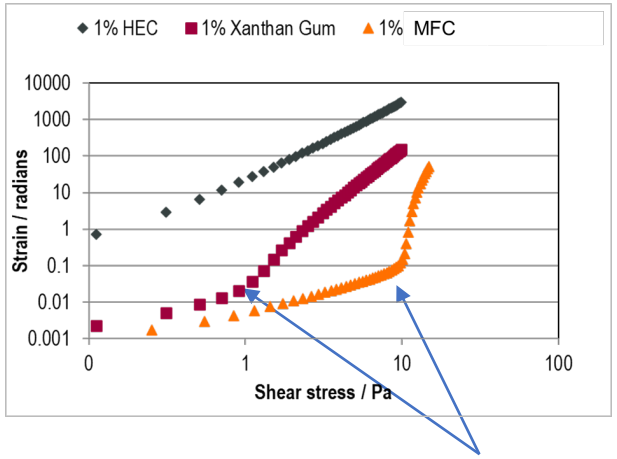




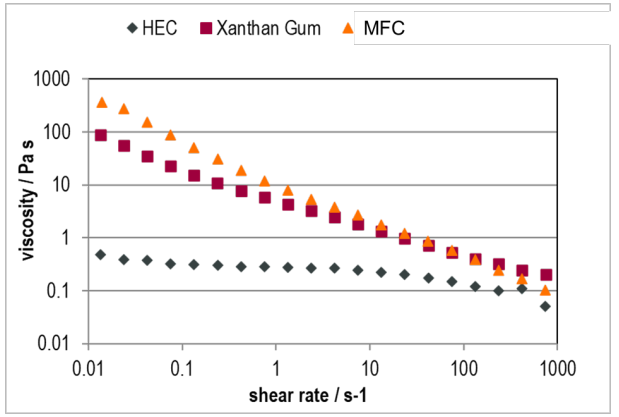



Mineral/ MFC composite
- GCC, kaolin
- BSK, HBK

## Suspension aids

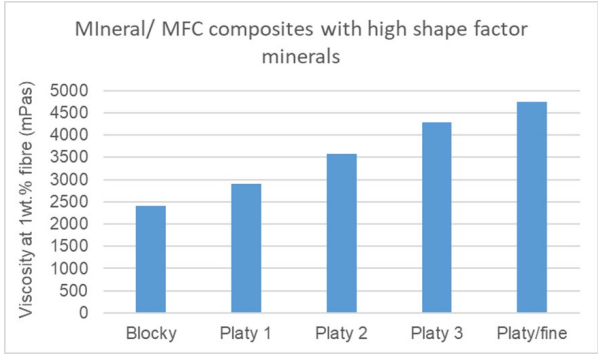



MFC gives very high yield stress




Low shear viscosity comparable with xanthan

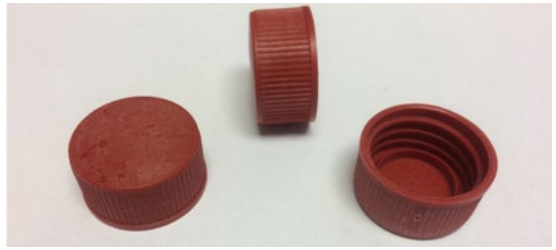
Mineral/ MFC composite
- Kaolin
- BSK, OCC



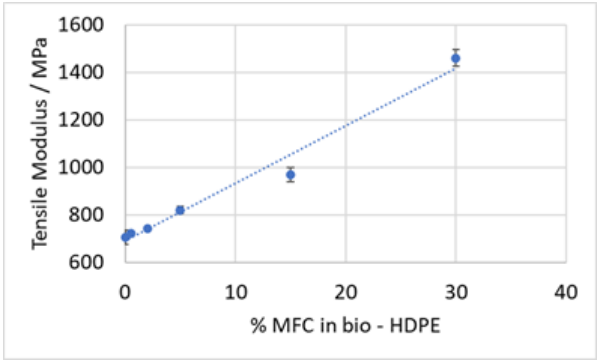

Viscosity modification at ~ constant tensile

# Applications: Reinforcement

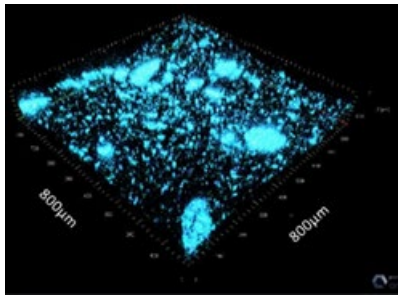
## Composites

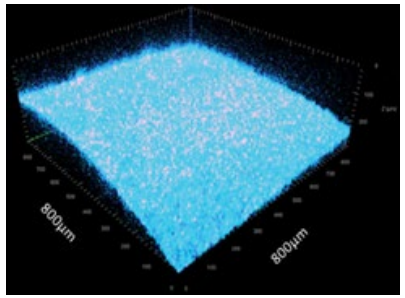


MFC allows moulding of fine features

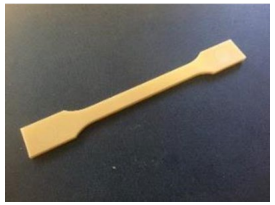



Well dispersed MFC is an effective reinforcement



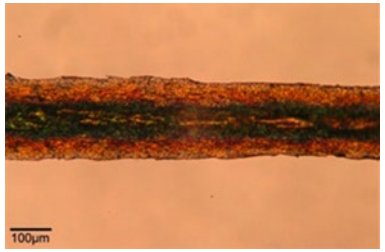



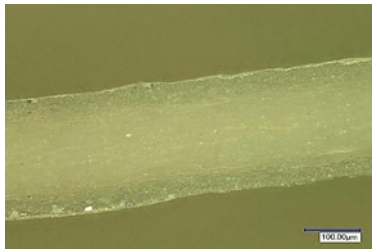

MFC can be evenly dispersed in polyolefin (fluorescent microscope scans – MFC in light blue)

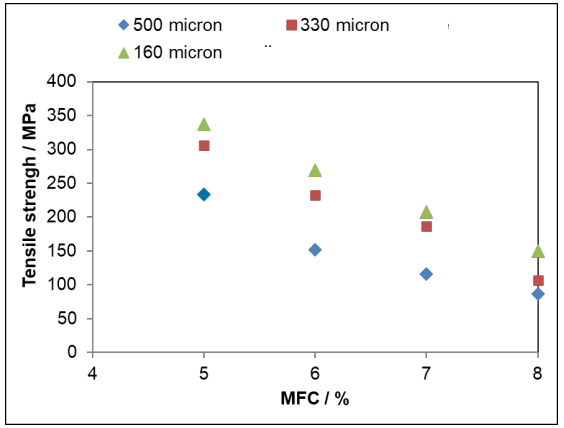


MFC
- No minerals
- Virgin fibres

## Textiles






- Extrusion of ~10% MFC through fine orifices
- High strength fibres after drying – fibril alignment
- Alignment increases with decreasing orifice size and suspension solids content

MFC
- No minerals
- Virgin fibres

# Regulatory status

**Current status**

**USA**

**EPA** – existing substance under TSCA. Not subject to reporting under EPA nano rule

**FDA** - Food contact clearance through FDA (5 wt.% fibrils in packaging board), FCNs 1582 and 1887

FDA GRAS – applied for as part of Vireo Advisors led consortium

**Canada**

Environment and Climate Change Canada – existing substance under CEPA

Health Canada opinion - "…we see no reason to object…to the use of [redacted] in food contact packaging, under conditions as described on the FDA website in the FCN 1582"

**China**

The National Health Commission of the People's Republic of China approved microfibrillated cellulose pulp (CAS 65996-61-4) as an additive in paper and paperboard used for contact with all types of food, subject to a maximum usage of 5% (based on the dry weight of fiber) and no specific migration level requirement

**Germany**

Acceptance has recently been confirmed for BfR XXXVI and XXXVI/2 at up to 5 wt.% fibrils

**Netherlands**

Recently advised that cellulose microfibers produced with calcium carbonate, kaolin and/or other permitted mineral fillers will be included in Chapter 2 (Paper and Board) of the Dutch commodities act regulation at up to 5 wt.% fibrils

# Running trials with low solids materials: 1

Production plant in the UK, 2000 dry metric tonnes pa of fibril capacity. Operational since Q4 2013: Slurry and press-cake product forms

## Slurry


## Press cake

# Running trials with low solids materials: 2

## Slurry

**Bottles (lab trials)**
10 litre (2.65 US Gallon) = 200 g (~8 oz) dry MFC
**Barrels (pilot trials)**
220 litre (60 US Gallon) = 4.4 kg (~10 lb) dry MFC
**IBC Tanks (pilot & full scale trials)**
1000 litre (265 US Gallon) = 20 kg (~44 lb) dry MFC
**Trucks/ ISO tanks (full scale trials)**
25 meter$^3$ (6600 US Gallon) = 500 kg (~1100 lb) dry MFC

**Largest shipments to date supplied for trials:**
80 Transitanks = 1600 kg (~3500 lb) dry MFC
7 Trucks = 3500 kg (~7700 lb) dry MFC

## Press cake

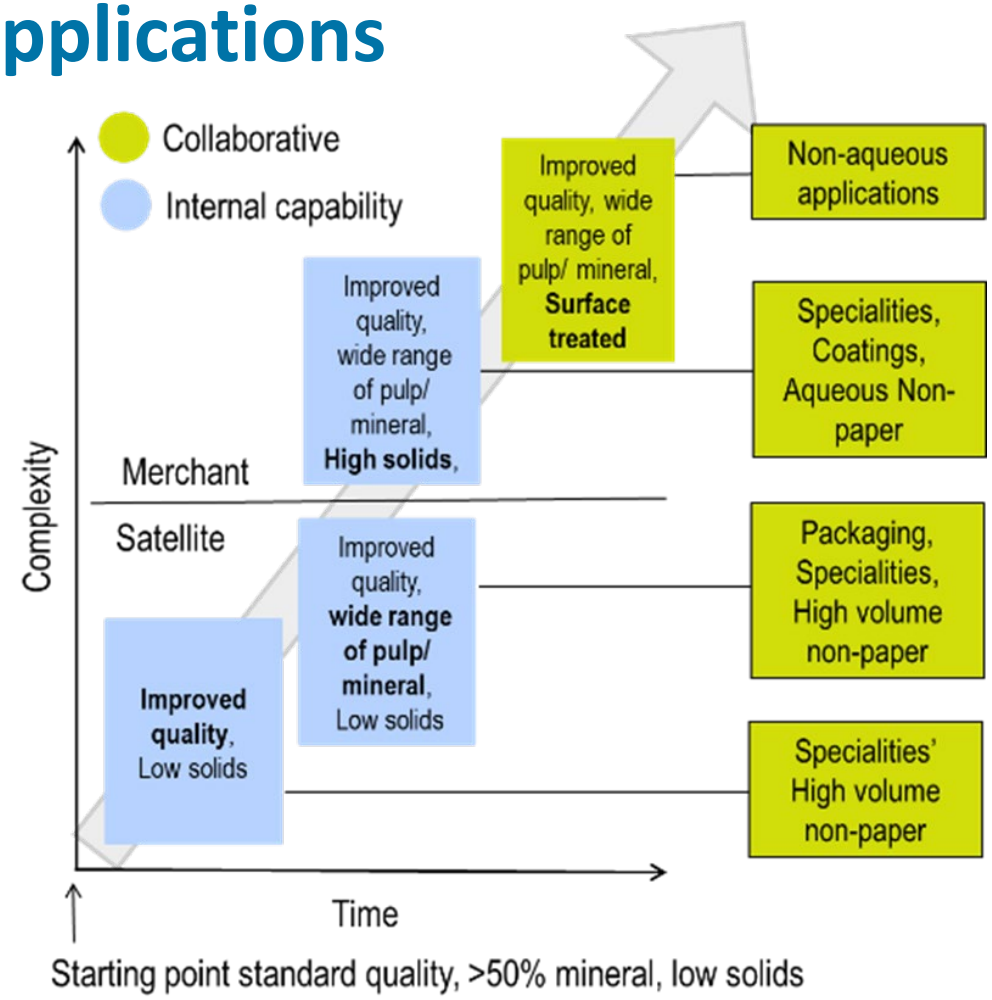
**IBC Bags (full scale trials)**
Bag weight ~ 1000 kg (~2200 lb) = 150 kg (~330 lb) dry MFC

**Largest shipments to date supplied for trials:**
292 bags = ~44 tonnes (~48 short tons) of dry MFC

## Make-down Unit

Redispersion from Press Cake to Slurry:
- ✓ Rapid Installation/Pack-up
- ✓ Throughput
- ✓ Quality
- ✓ Safety

# Challenges for the future : Product development in an expanding range of applications




- Platform technologies largely developed
- Patent estate largely in place
- Wide range of posssible applications beyond original targets
- Collaborative development programmes in UK, EU and US

# Conclusions

- MFC and mineral/ MFC composites are produced using a cost-effective, robust process and have proven full-scale availability
- MFC and mineral/ MFC composites can be produced using a wide range of minerals and pulps. Variations in the selction of pulp and mineral allow the formulator to select in favour of a wide range of properties
- Recycled pulp streams can be used
- Recent improvements in product peformance arising from process optimisation
- We believe that MFC and mineral/ MFC composites are an important additive for a wide range of applications

# Thank you for your attention

We are grateful to TAPPI for the opportunity to present this work

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