Sustainable mineral/ microfibrillated cellulose composite formulation additives: Properties and uses

David Skuse

FiberLean Technologies Ltd

RSC Particles in formulations meeting

December 16, 2020

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The company

- Produce a mineral/ microfibrillated cellulose composite
- FiberLean Technologies Limited is a UK listed company
- Headquarters – Par Moor Centre, Par, Cornwall
- ~65 Employees
- 50:50 JV between Imerys and Omya

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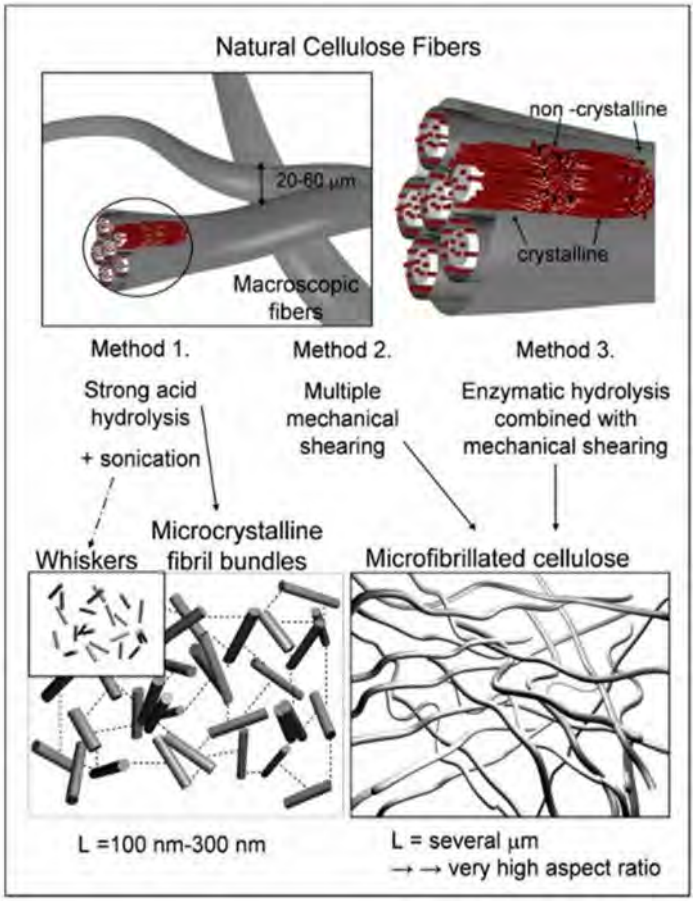
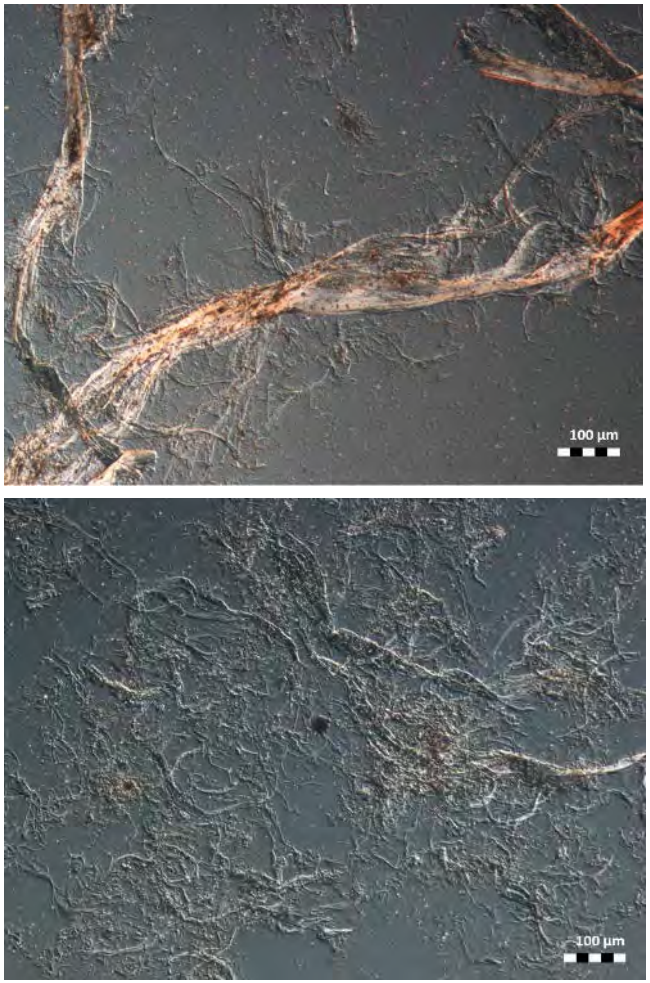
The product: Microfibrillated cellulose



Picture by Pääkkö, Ankerfors et al, Biomacromolecules 2007,8 1934-1941



Using fibre property measurements to predict the tensile index of microfibrillated cellulose nanopaper, L. Taylor, J. Phipps, S. Blackburn, R. Greenwood and D. Skuse, Cellulose (27, 6149 – 6162 (2020)

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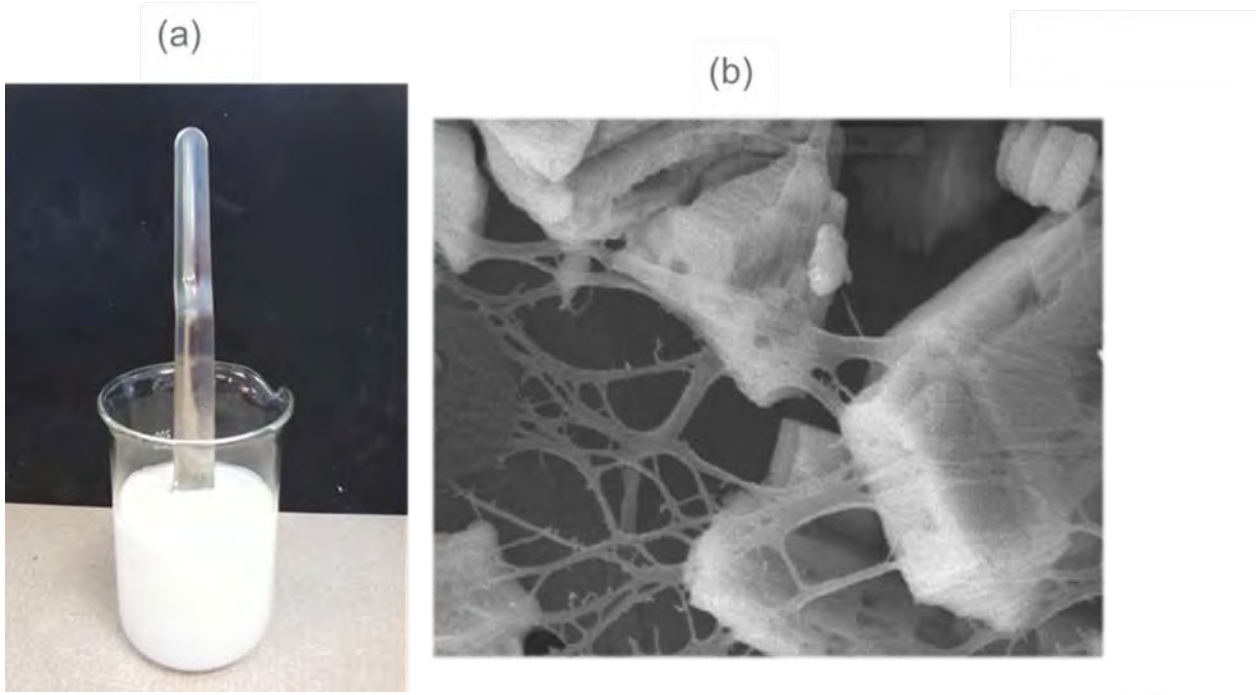
The product: Mineral/ microfibrillated cellulose (MFC) composites

- A network structure of cellulose fibrils and micron sized minerals
- Viscous suspension with fibril solids ~1-2 % **(Produced in satellite production plants at customer locations)**



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

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The production process: Mineral assisted fibrillation of cellulose pulp

- Processsing and handling of mineral/ MFC composites are dominated by the high viscosity of MFC arising from presence of high surface area hydrophillic fibrils
- **Cost effective** grinding-based method to produce mineral/ MFC composites from minerals and cellulose
  - 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**
- **Commercialised** as **FiberLean MFC®**
- 10 000 dry metric tonnes pa of fibril capacity (40 000 dry metric tonnes of mineral/ MFC composite) operational across three continents
- Further capacity under construction

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MFC – Utility for increased bonding in fibre-based structures, viscosification, reinforcement.....

- Printing and writing paper
- Cellulosic packaging
- Paints and coatings
- Functional materials
- Adhesives
- Filtration media
- Food
- Additive/thickener
- Coating
- Packaging
- Construction materials
- Ceiling tiles
- Medium density board
- Cement additives
- Drilling fluids
- 3D printing
- Nonwovens
- Flexible and printed electronics
- Batteries
- Energy storage
- Medical
- Implants
- Scaffolds
- Wound dressings
- Bone graft substitute

Formulation: Minerals

Structure performance relationships

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
- ……

- **Applications**
- Paper/ Packaging
- Building materials
- Coatings/ inks
- Oil field
- Food and beverage
- Non-wovens
- Composites
- Electrical/ electronic
- Abrasives
- Filtration
- Ceramics
- ……

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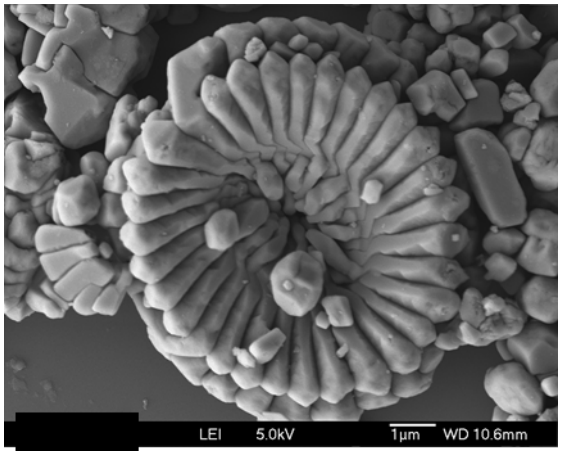
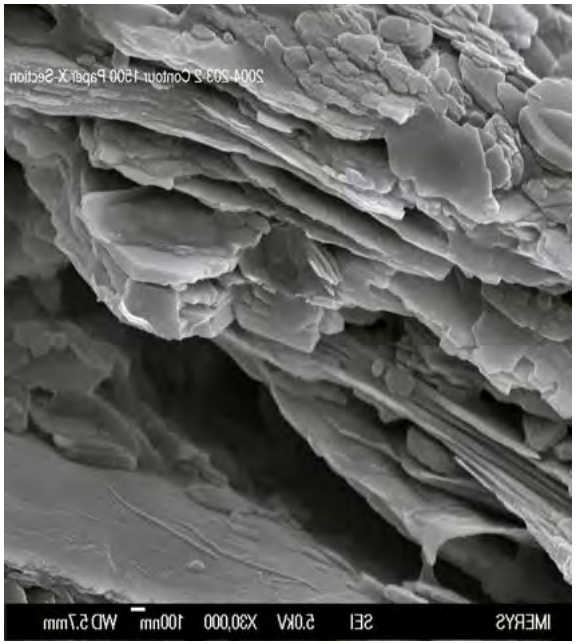
Formulation: Minerals

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





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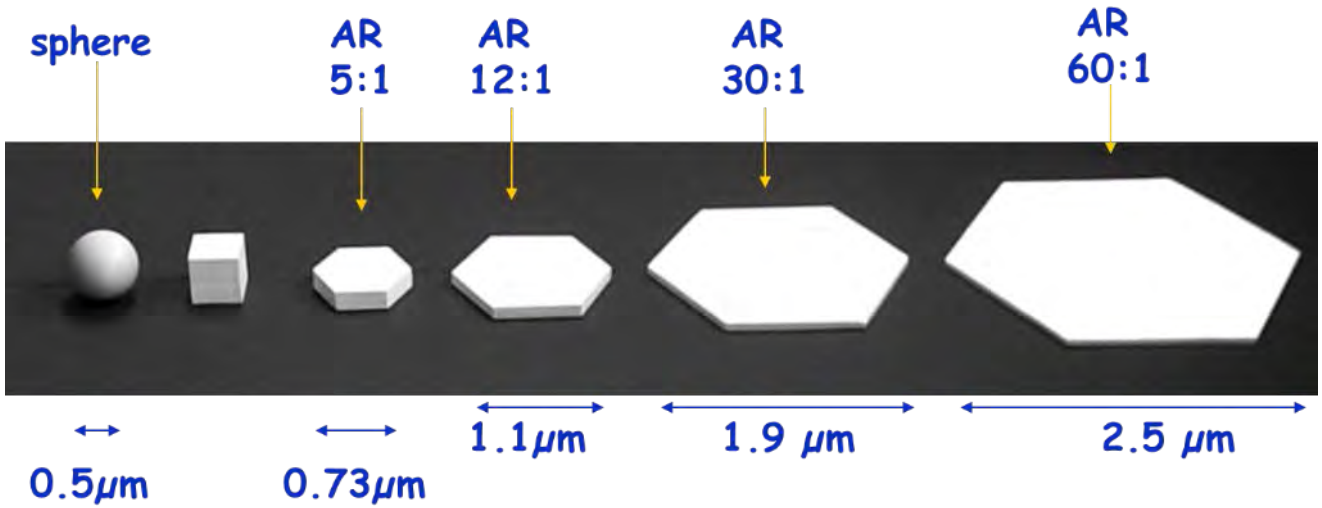
Characterisation and dispersion: Minerals

Particle size – sedimentation - but with care



All the above particles have the same esd (0.5 μm)

Particle size and shape characterisation : Current technology and practice, Hart J., Zhu Y. and Pirard E., in Advances in the characterisation of industrial minerals, ed. Christidis G, Mineralogical Society of Great Britain and Ireland, ISBN 9780903056359, 2010

Parslow, K. & Jennings, B.R. (1988) Particle size measurement: the equivalent spherical diameter. Proc. Roy. Soc. A 419, 137–149.

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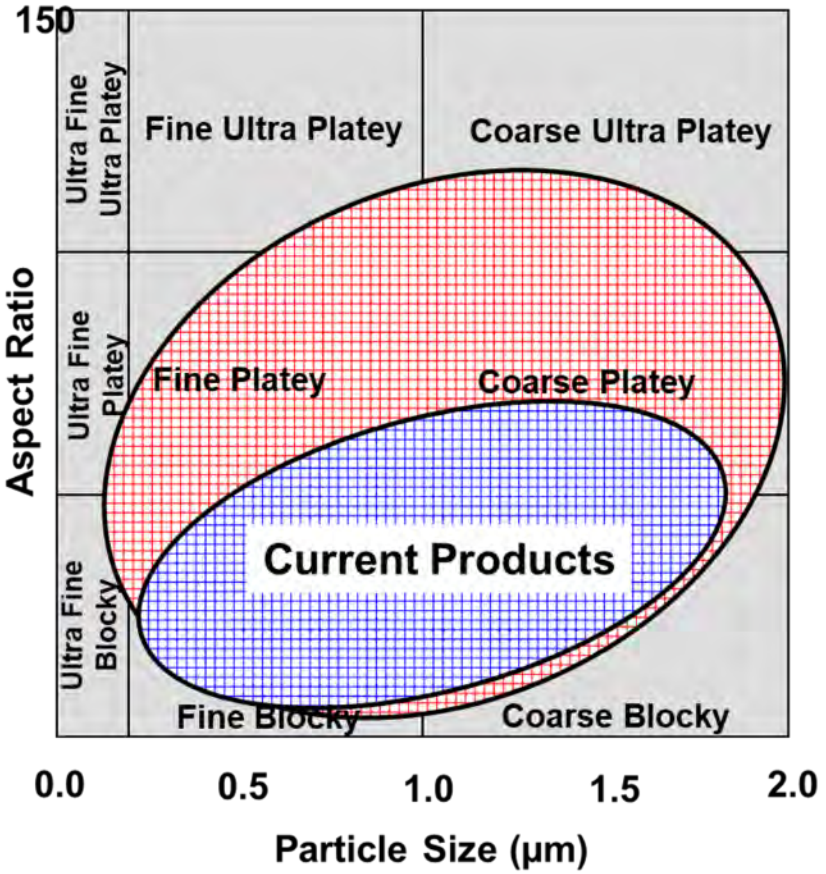
Characterisation and dispersion: Minerals

Particle shape

PANACEA device

- Developed in-house at Imerys
- Particles are aligned in laminar flow
- Conductivity changes with time after flow is stopped as particle orientation randomises
- Proportional to shape factor
- Has allowed development of a range of kaolin products having different shape factors



Paynter, PhD thesis, University of Bristol, 1998

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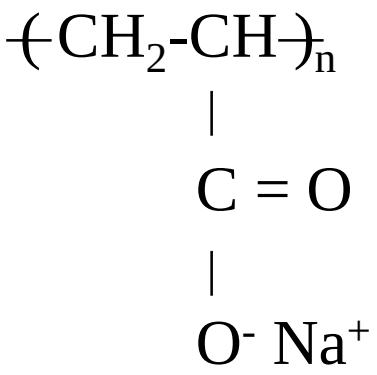
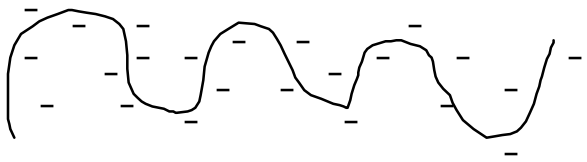
Characterisation and dispersion: Minerals

Particle dispersion: Sodium polyacrylate



Synthesized by free radical polymerization of acrylic acid and subsequent neutralization with sodium hydroxide

Polyanion



Extensive optimization: molecular mass, dispersity, neutralisation, co-monomers, end groups, regulatory approvals

Electrosteric mechanism
Optimisation by minimising **non-adsorbed** dispersant

K.R. Rogan, A.C. Bentham, I.A. George and D.R. Skuse, Colloid Polym. Sci., 272, 1175-1189 (1994). Colloidal stability of calcite dispersion treated with sodium polyacrylate

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Formulation: Fibrils and fibres

Structure performance relationships

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
- ……

- **Applications**
- Paper/ Packaging
- Building materials
- Coatings
- Oil field
- Food and beverage
- Non-wovens
- Composites
- Electrical/ electronic
- ……

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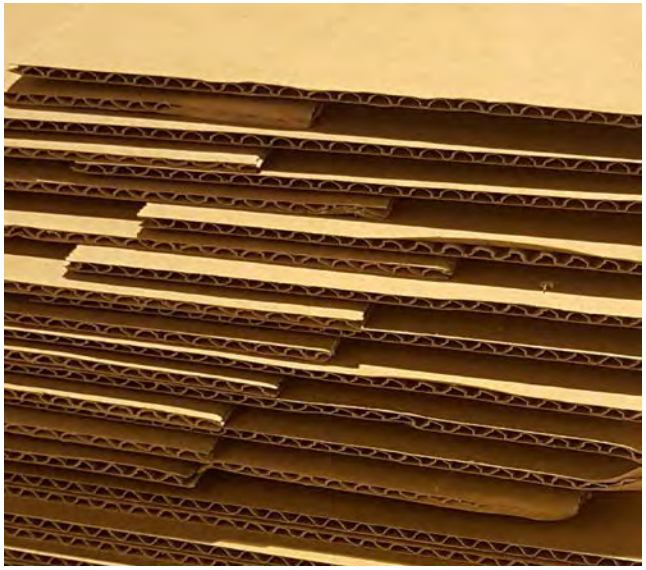
Formulation: Fibres

Fibre sources

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



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Characterisation: Fibres

- Suite of industry standard tests
- Fibre analyser
- Dispersion – variety of additives and surface modifications usually introducing anionic charge

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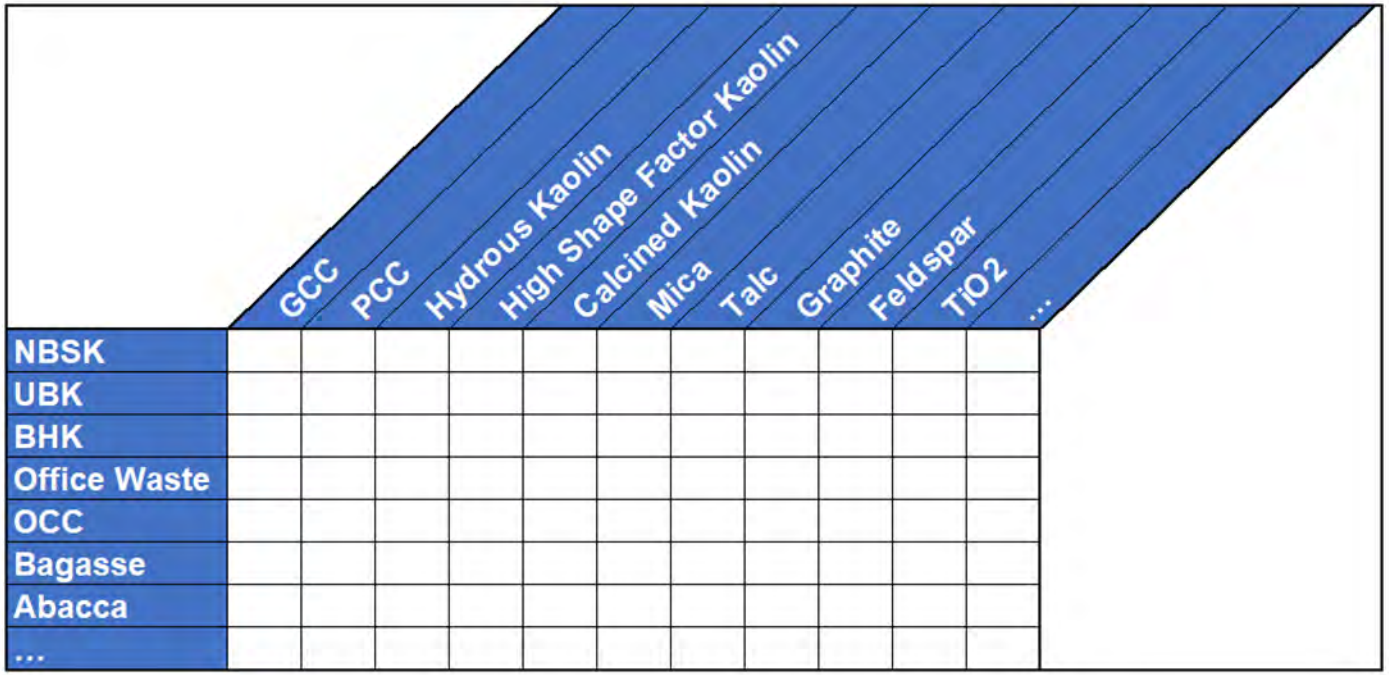
Formulation: Mineral fibril composites

- There are a multitude of options available to the formulator



- The selection of fibre and mineral type, as well as the ratio between them, is tailored for each application.

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Characterisation: Mineral/ MFC composites

- Fiber analyser
  - *Effects of cellulosic nanofibrils on papermaking properties of fine papers, D. A. Johnson, M. A. Paradis, M. Bilodeau, B. Crossley, M. Foulger, and P. Gélinas, TAPPI Journal, June 2016*
- Laser light scattering
  - *From paper pulp to plastic – techniques that control nanocellulose fiber quality and improve drying efficiency, GEA webinar, 2 December 2020*
- Detailed physico chemical characterisation
  - *Physical, chemical and toxological characterization of fibrillated forms of cellulose using an in vitro gastrointestinal digestion and co-culture model, Shatkin et al, Toxicology Research, 9 (3), June 2020, 290-301*
- Performance based tests
- SEM – micro and nano components
  - Comparative fibril diameter measurement for regulatory clearances

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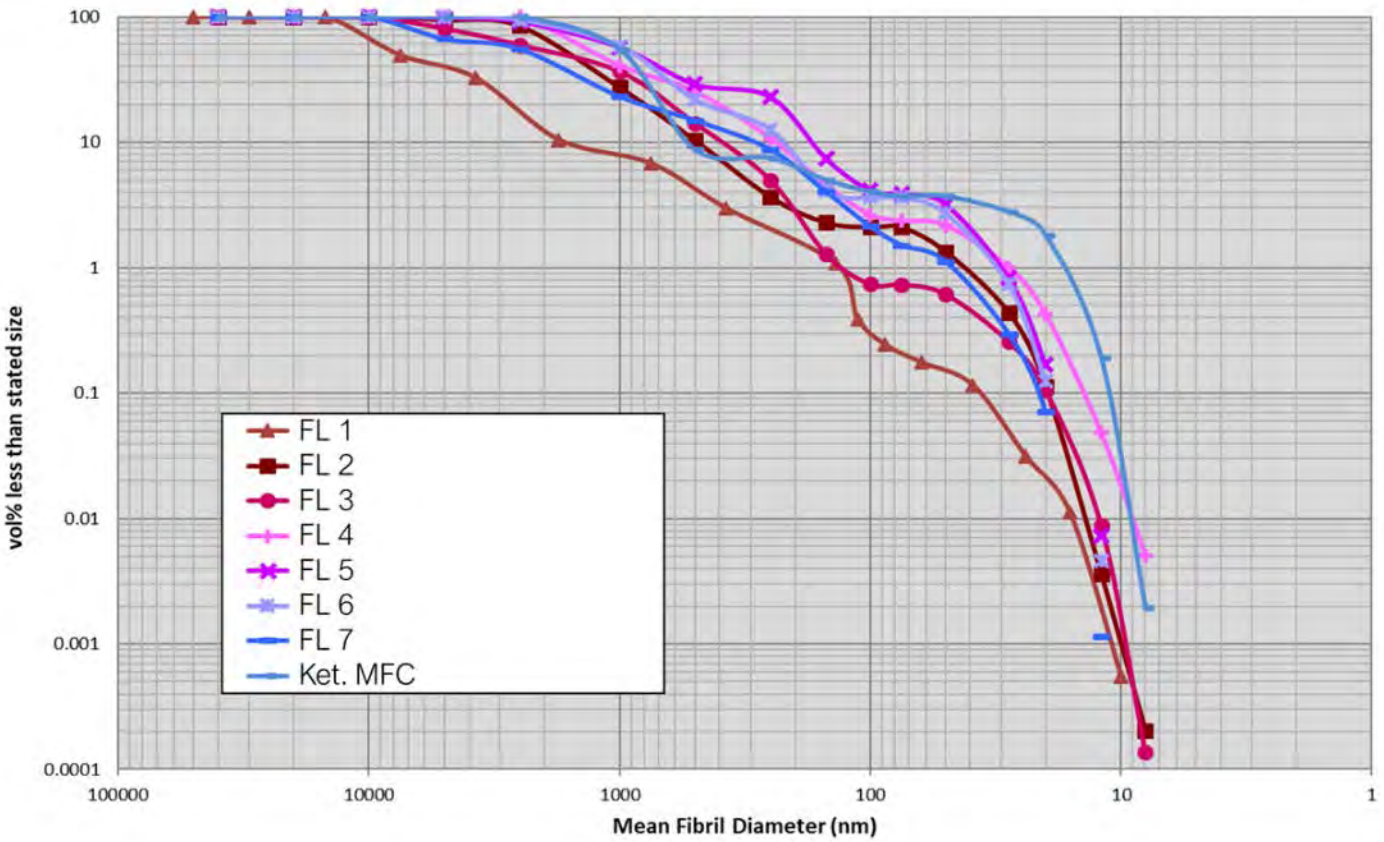
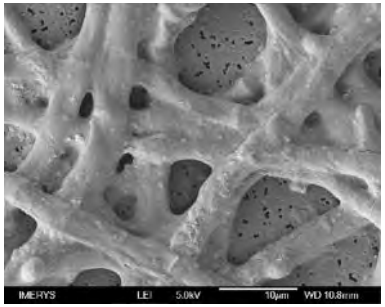
Characterisation: Mineral/ MFC composites





Comparision of FiberLean MFC fibrils with food grade MFC shows similar fibril width

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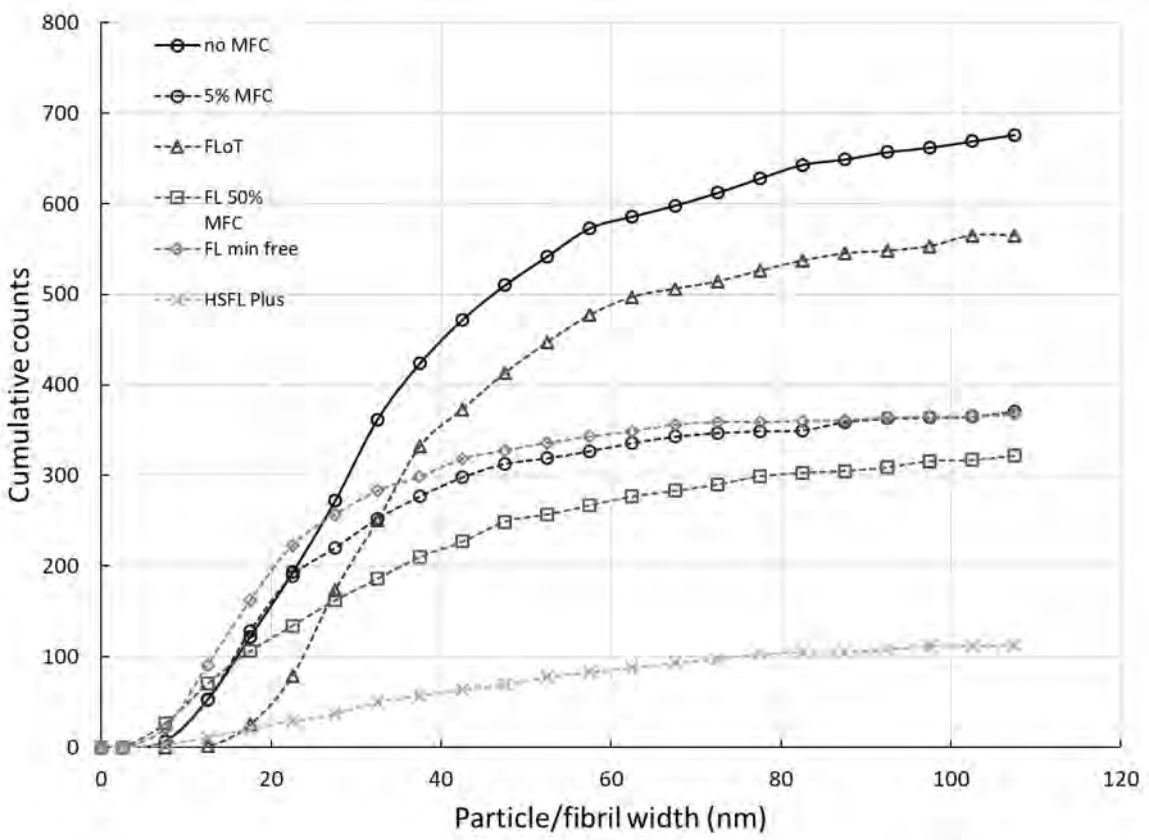
Characterisation: Mineral/ MFC composites

SEM based extraction study of fibrils from MFC containing sheets and controls shows that there is less fibril migration in MFC containing sheets than controls



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Regulatory clearances are essential for many target applications

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 FiberLean 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

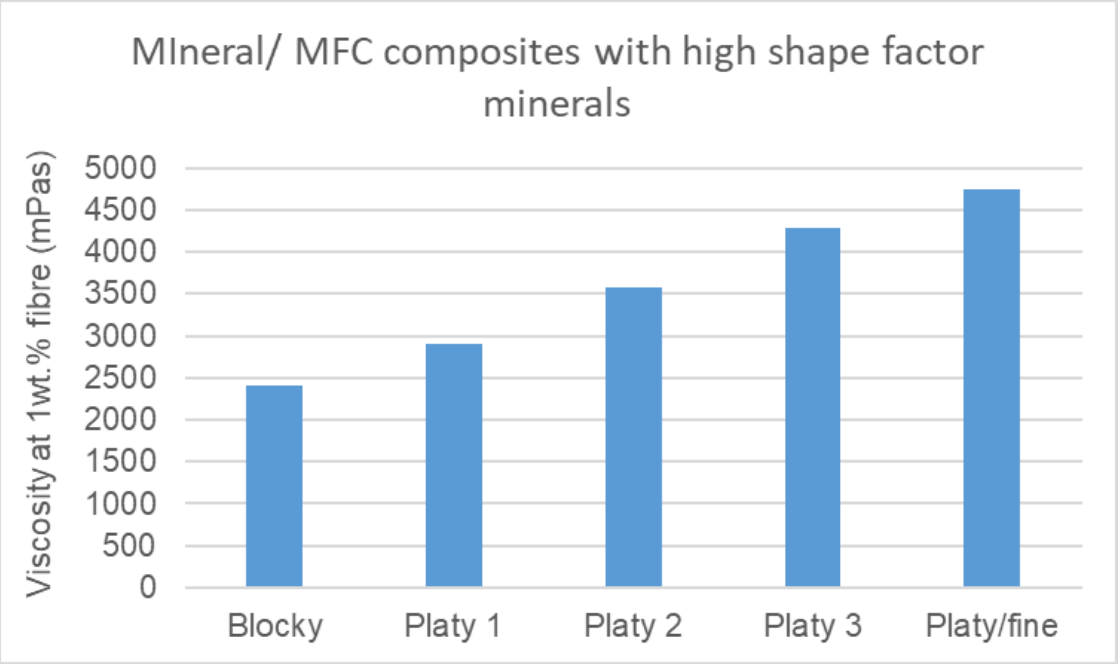
Germany

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

Formulation: Viscosity modification at ~ equivalent tensile properties



- 50% NBSK/ 50% mineral/ MFC composites
- Can control viscosity with choice of mineral shape factor.
- Low shape factor for high solids application
- High shape factor for high viscosity

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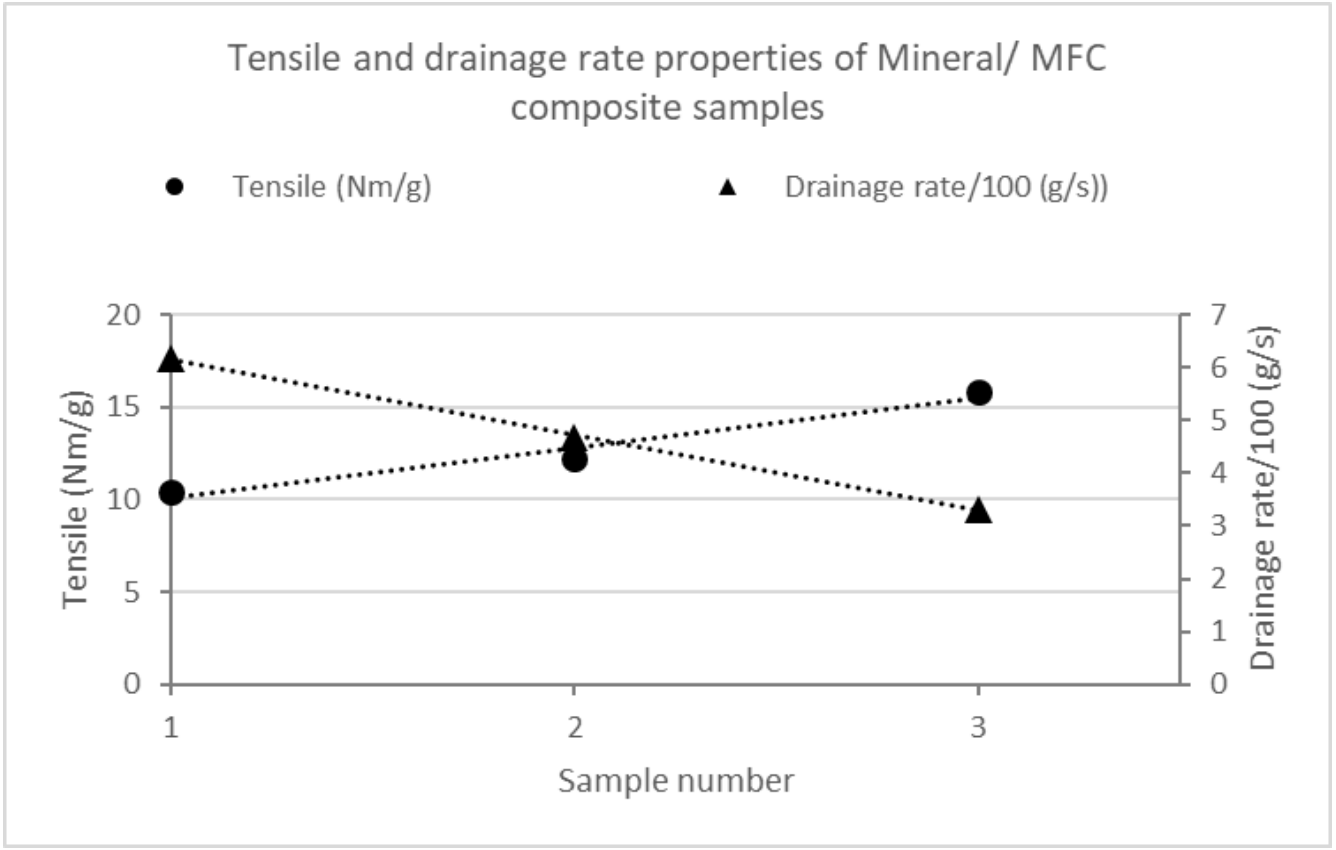
Formulation: Drainage and tensile behaviour



- 50% NBSK/ 50% mineral/ MFC composites
- Can vary process conditions to meet drainage constraints in application

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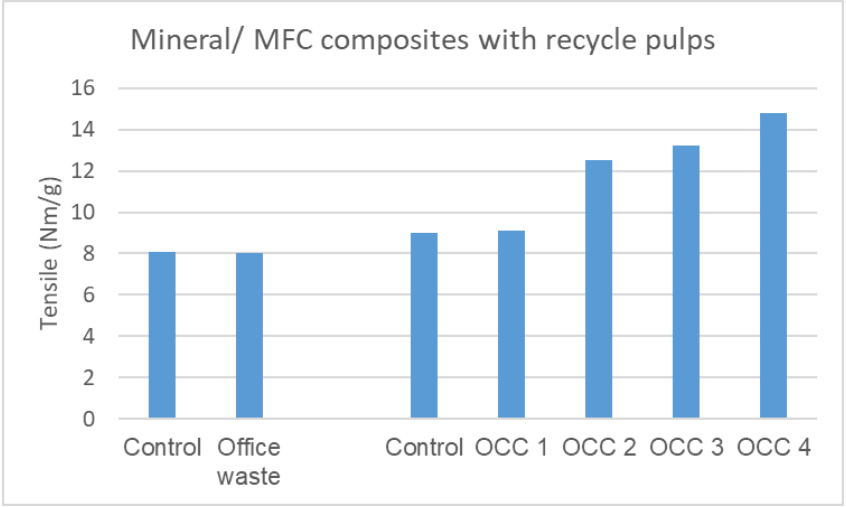
Formulation: Circularity

- FiberLean Mineral/ MFC composites prepared from mixed office waste and Old Corrugated Cardboard (OCC)
- Tensile properties at ~ equivalent to/ better than virgin Northern Bleached Softwood Kraft (NBSK) pulp controls



Mixed office waste feed

50% OCC/ 50% kaolin mineral/ MFC composite (right) and control with NBSK

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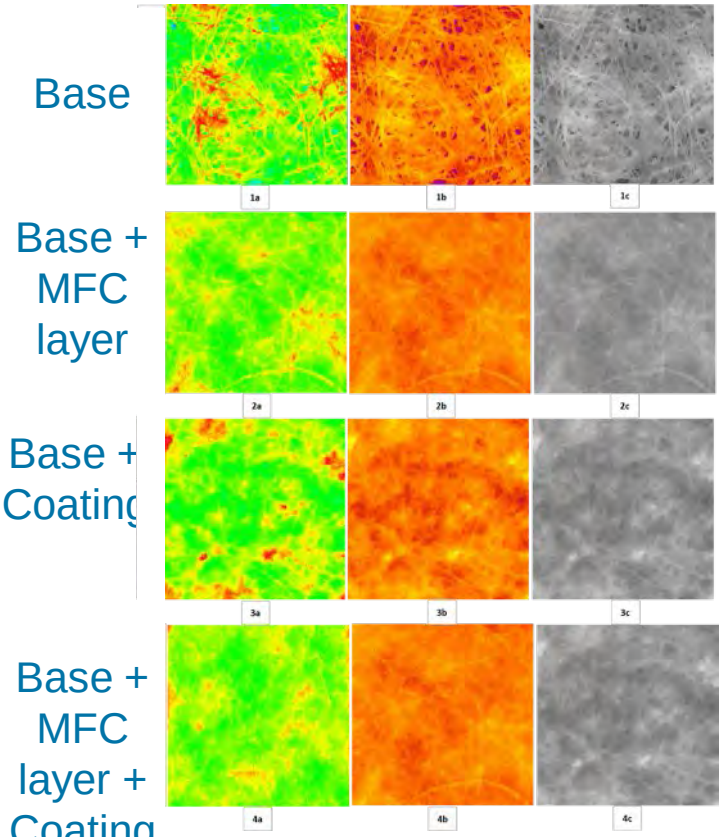
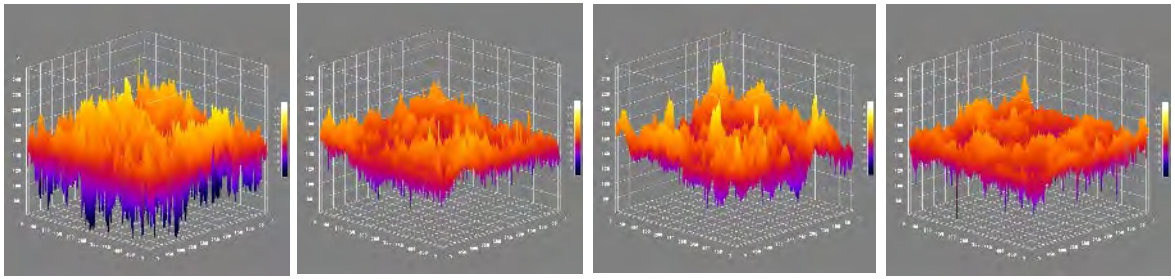
Formulation: Barriers - Single use plastic replacement





Base | Base + MFC layer | Base + Coating | Base + MFC layer + Coating

Test	Base	Base + MFC layer	Base + Coating	Base + MFC Layer + Coating
COBB g m $^{-2}$	50	58	46	**1**
Kit	<1	**16**	3	16
MVTR g m $^{-2}$ day $^{-1}$	272	239	**194**	**5**
jMVTR g m $^{-2}$ day $^{-1}$	1031	992	**351**	**23**

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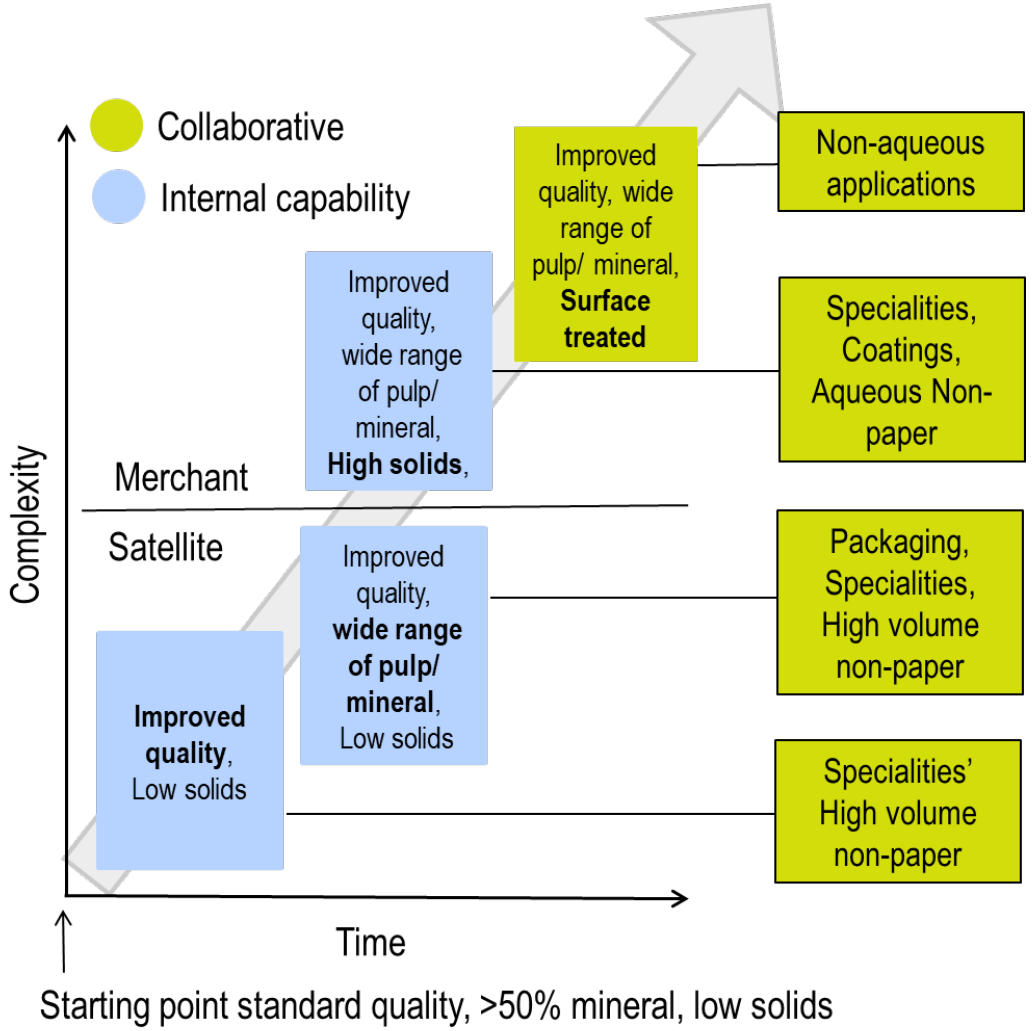
Challenges for the future



- Platform technologies largely developed
- Patent estate largely in place
- Enormous range of posssible applications beyond original paper targets

- Looking to work collaboratively on applications and characterisation to:
  - Share cost/ risk
  - Access expertise beyond our own
  - Develop a network of partners

- UK, EU and US funding programmes

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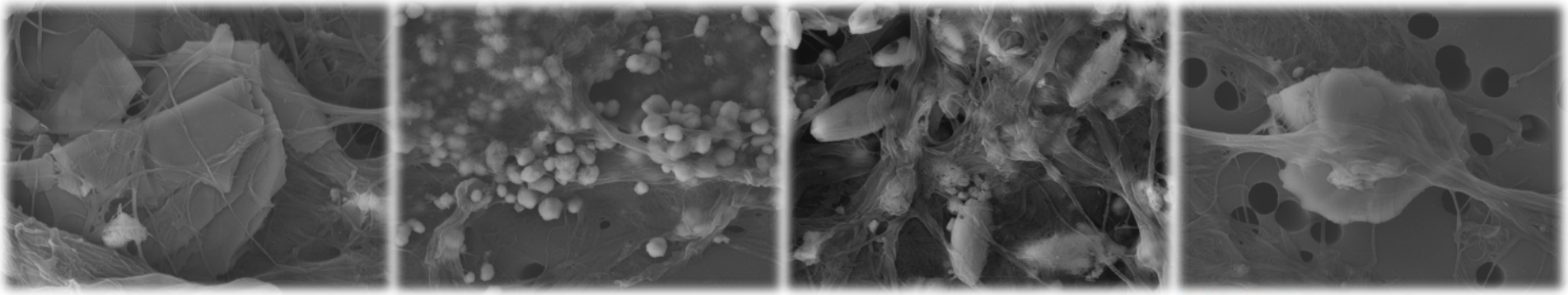
Conclusions

- Mineral/ MFC composites are produced using a cost-effective, robust process and have proven full-scale availability
- 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
- We believe that mineral/ MFC composites are an important additive for a wide range of applications
- These mineral/ MFC composite materials have been commercialised as FiberLean MFC ®



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Presented by:

David Skuse

VP Technology, FiberLean Technologies Ltd

david.skuse@fiberlean.com

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