Influence of Fibril Morphology on the Barrier Properties of Microfibrillated Cellulose Coatings and Films

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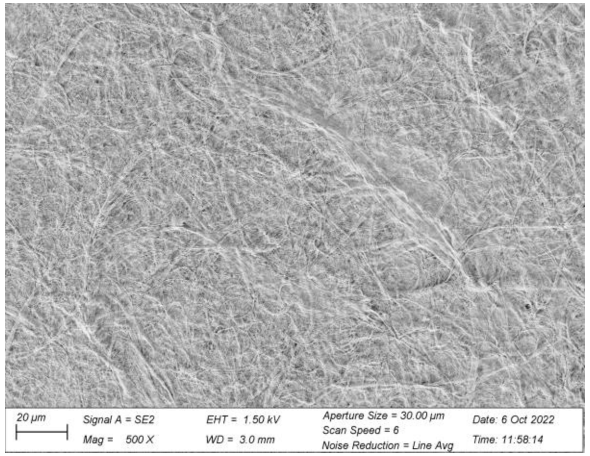
Background

- Up to 90 Mt of plastic waste per year may reach our waters by 2030. (Borrelle *et al.* 2020)

- Per or poly fluoro alkyl substances (PFAS) can be used in food packaging to give grease or water resistance to paper or cardboard. (H. Schwartz-Narbonne *et al.* 2023)

- Microfibrillated cellulose (MFC) could provide a more sustainable packaging alternative since layers of MFC can slow transport of oxygen or oil. (Lavoine *et al.* 2012)

Vanessa P, Strawberries in Packaging Containers, https://www.pexels.com/photo/strawberries-in-packaging-containers-2629173/ . License: [Free Stock Photo & Video License - Pexels]



SEM image of dewatered MFC suspension

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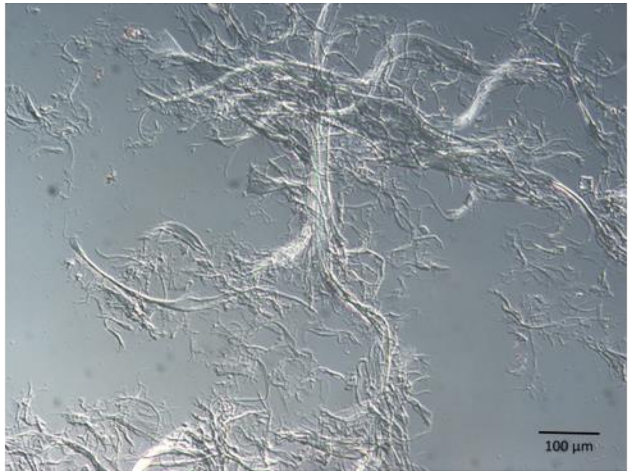
S. B. Borrelle, J. Ringma, K. L. Law, C. C. Monnahan, L. Lebreton, A. McGivern, E. Murphy, J. Jambeck, G. H. Leonard, M. A. Hilleary, M. Eriksen, H. P. Possingham, H. De Frond, L. R. Gerber, B. Polidoro, A. Tahir, M. Bernard, N. Mallos, M. Barnes and C. M. Rochman, *Science,* 2020, **369**, 1515-1518.
H. Schwartz-Narbonne, C. Xia, A. Shalin, H. D. Whitehead, D. Yang, G. F. Peaslee, Z. Wang, Y. Wu, H. Peng, A. Blum, M. Venier and M. L. Diamond, *Environmental Science & Technology Letters*, 2023, **10**, 343-349
N. Lavoine, I. Desloges, A. Dufresne and J. Bras, *Carbohydrate Polymers*, 2012, **90**, 735-764.

How does MFC degree of fibrillation affect barrier properties?

- MFC can be polydisperse with a large size distribution, making characterisation difficult. (Kangas *et al.* 2014)
- Increasing mechanical processing to create smaller fibrils can improve oxygen barrier properties. (Padberg *et al.* 2016)
- This research discusses how the extent of separation of cellulose fibres into fibrils affects the barrier properties of MFC films and coatings and whether any resulting decrease in crystallinity has an effect.



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H. Kangas, P. Lahtinen, A. Sneck, A.-M. Saariaho, O. Laitinen and E. Hellén, *Nordic Pulp & Paper Research Journal*, 2014, **29**, 129-143.

J. Padberg, W. Bauer and T. Gliese, *Nordic Pulp & Paper Research Journal*, 2016, **31**, 548-560.

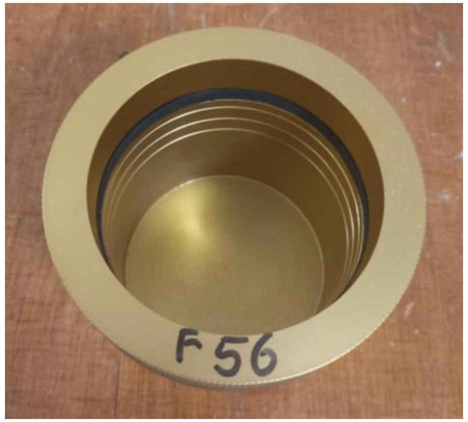
Methodologies

Making MFC films or coatings:

- MFC was coated onto base paper from a dilute suspension using vacuum filtration and dried at 93°C and 1 bar vacuum pressure in Rapid-Köthen handsheet driers.
- This is a lab scale method to mimic an industrial process.
- MFC films were made in the same way but a SEFAR nylon filtration mesh with 11 µm pore size was used in place of the base paper.

Barrier testing:

- Air permeability (Bendtsen porosity test)
- Kit testing (grease resistance)
- Water vapour transmission rate (films only) (WVTR)
- Heptane vapour transmission rate (HVTR)- MFC can form an effective barrier to heptane vapour (Kumar *et al.* 2016)



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V. Kumar, A. Elfving, H. Koivula, D. Bousfield and M. Toivakka, *Industrial & Engineering Chemistry Research*, 2016, **55**, 3603-3613.

MFC Characterisation

- This research aims to find what type of MFC makes the most effective barrier layers.

- To know this, there must be a way to compare different MFC samples. This is difficult and several characterisation methods are necessary. (Kangas *et al.* 2014)

- Characterisation methods used in this research:
  - Fibre image analyser
  - Optical microscopy of MFC suspensions
  - SEM images of dewatered MFC suspensions (selected samples)
  - Tensile index of 20% MFC, 80% mineral sheets (Fiberlean Technologies method)
  - XRD to measure crystallinity index

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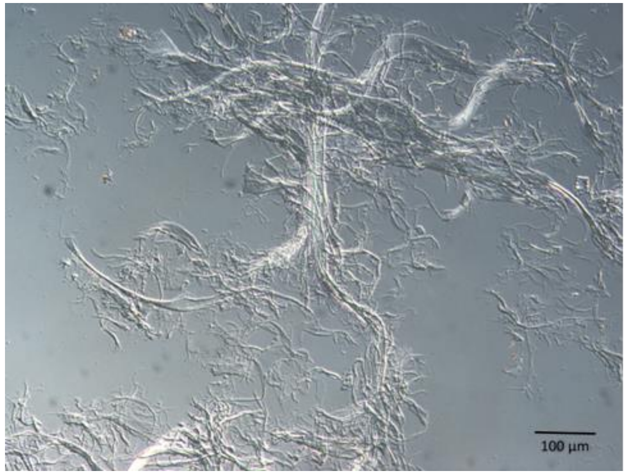
H. Kangas, P. Lahtinen, A. Sneck, A.-M. Saariaho, O. Laitinen and E. Hellén, *Nordic Pulp & Paper Research Journal*, 2014, **29**, 129-143.

Effect of increasing fibrillation on grease resistance and heptane vapour barrier

10 g m^{-2} of MFC with increasing fibrillation from refined pulp to finely dispersed MFC was coated onto base paper and the HVTR and Kit number were measured.



HVTR/ g m^{-2} day^{-1}	2146 ± 134	121 ± 8	17 ± 12
Kit number	1	4	12

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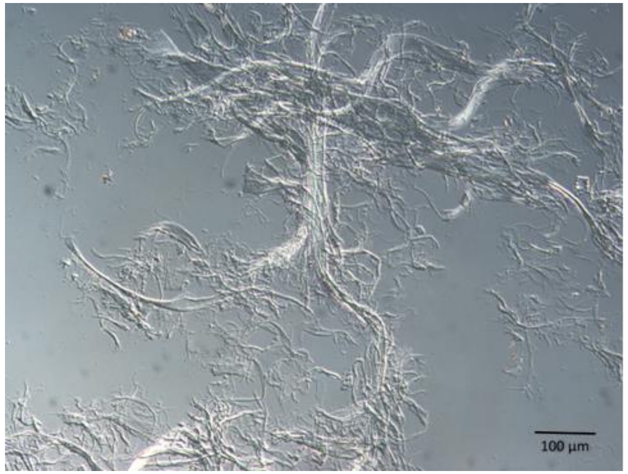
Increasing Kit number = increasing grease resistance.

HVTR= heptane vapour transmission rate.

Effect of increasing fibrillation on water vapour barrier

50 g m^{-2} films of MFC with increasing fibrillation from refined pulp to finely dispersed MFC were made and WVTR (water vapour transmission rate) was measured.



WVTR/ g m^{-2} day^{-1}	213 ± 4	82 ± 2	96 ± 1

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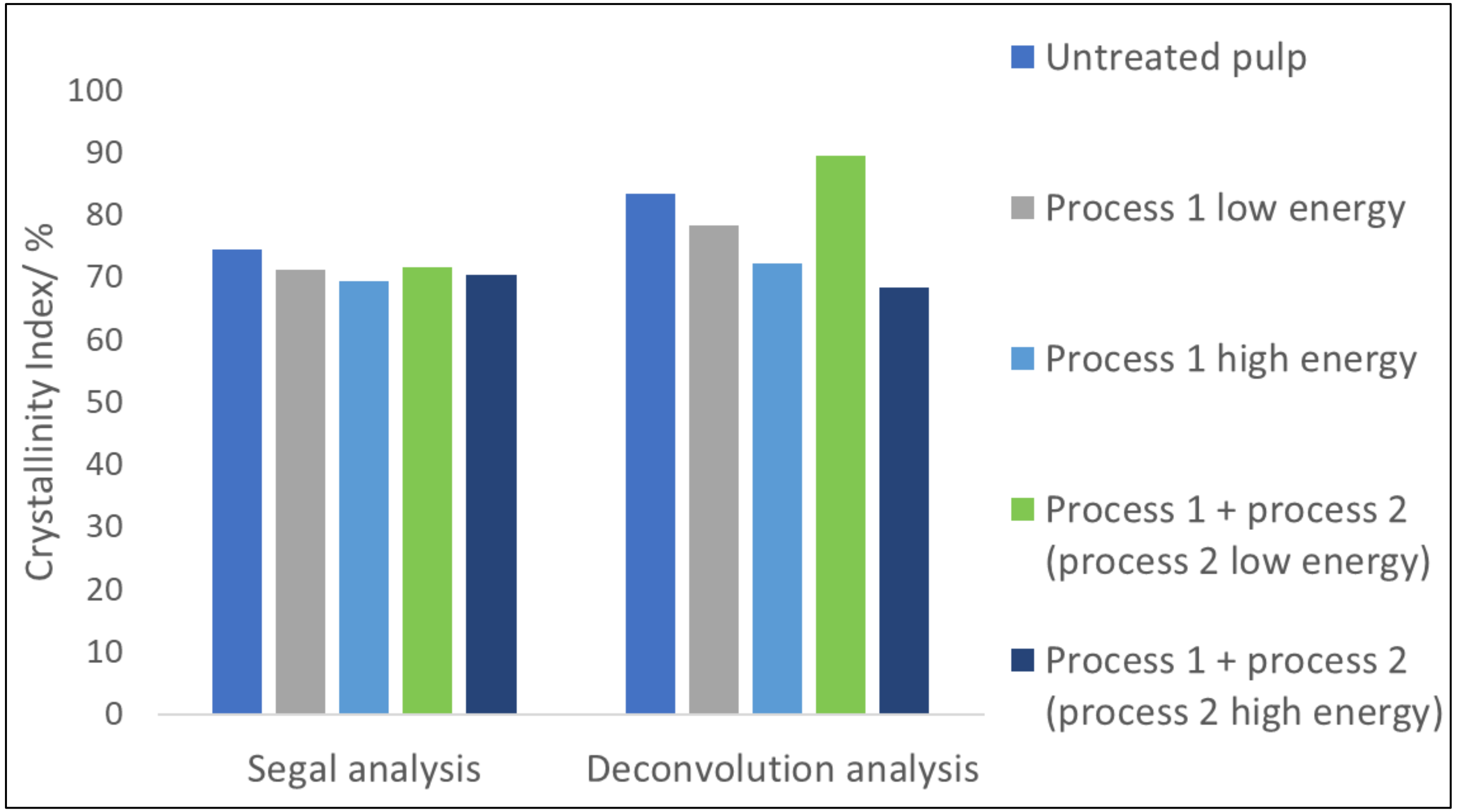
Effect of MFC process on cellulose crystallinity

Crystallinity index of MFC measured in this study by XRD on MFC films



Segal analysis performed using Crystal Diffract software

- A small decrease in crystallinity index is seen from the separation of fibres into fibrils. However, the decrease in crystallinity did not negatively affect grease or heptane vapour barrier properties.
- The change in crystallinity may account for the small increase in WVTR of films as fibrillation increased.

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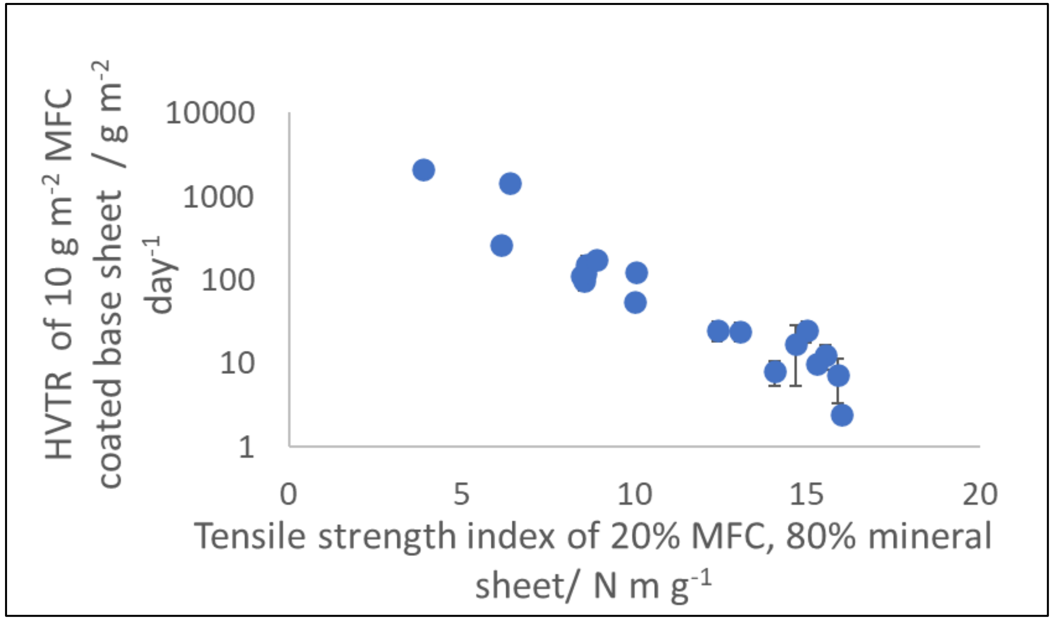
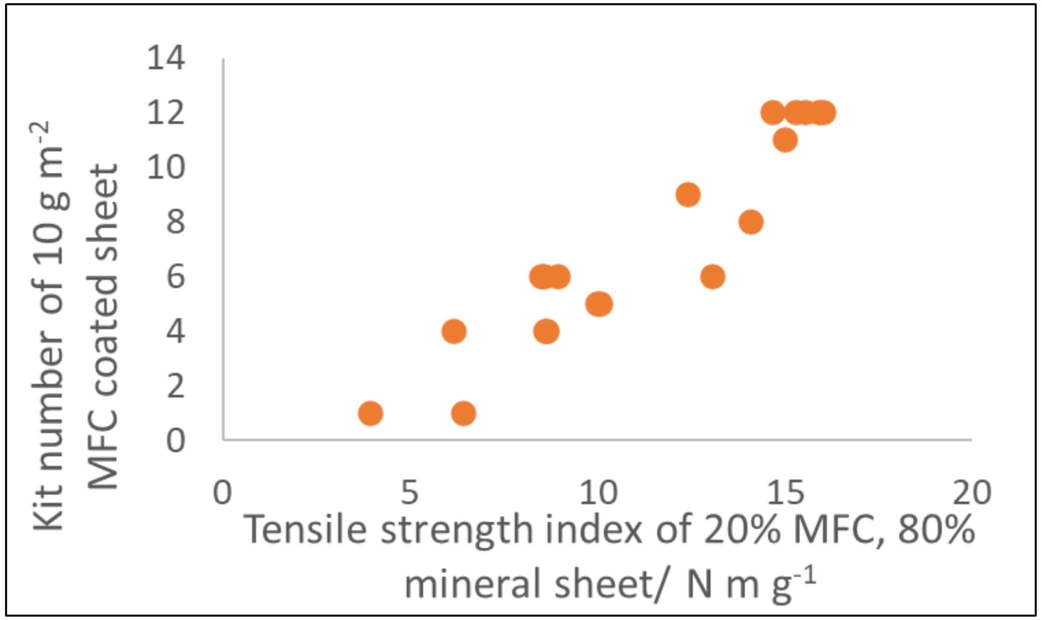
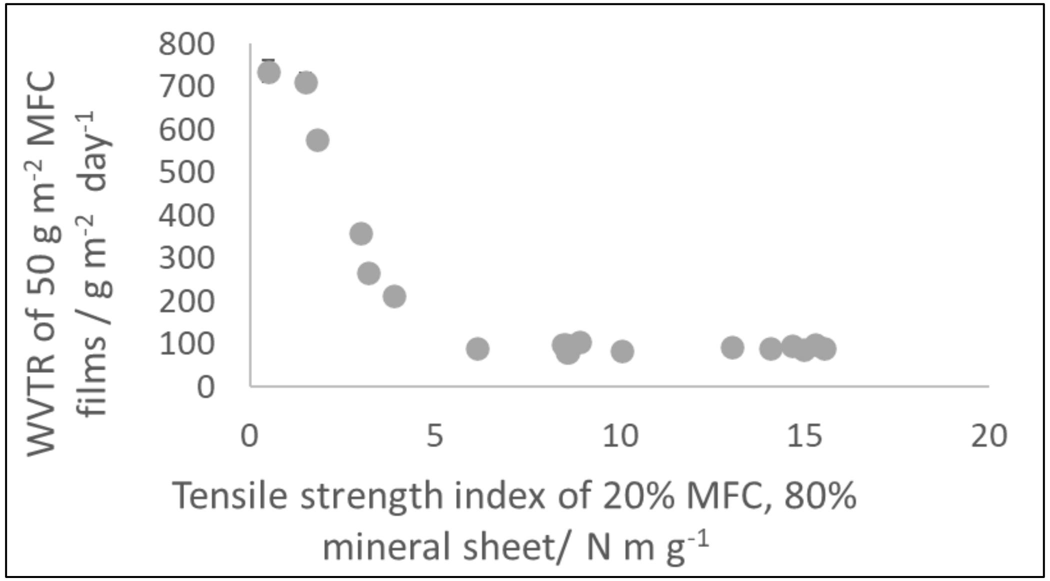
S. Park, J. O. Baker, M. E. Himmel, P. A. Parilla and D. K. Johnson, *Biotechnology for Biofuels*, 2010, **3**, 10





- Tensile strength index of a sheet made from 80% mineral, 20% MFC is useful to predict how effective an MFC sample is as a barrier layer.

- Tensile strength of paper depends partly on the number and strength of hydrogen bonds which is also likely to improve barrier properties. (Lindström, 2017)



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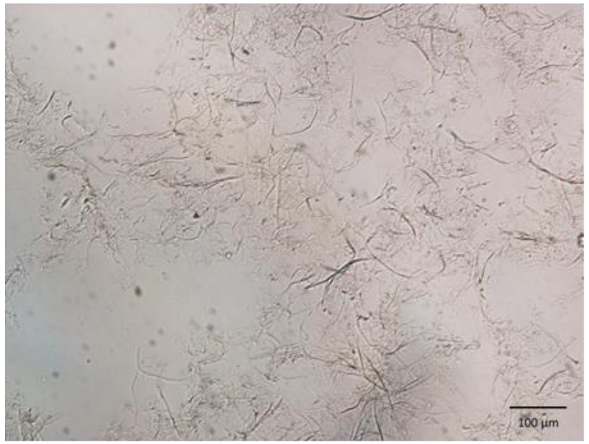
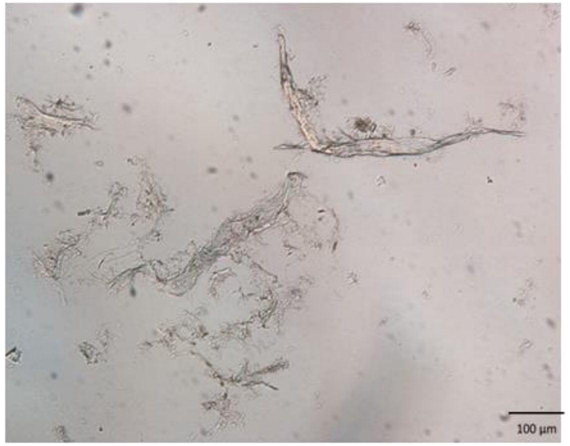
Can increasing coat weight make up for using a less fibrillated MFC? Part 1



MFC 1

MFC 2



MFC 3

Fines B/ %	72.84	16.53	6.86
Lc(l)/ mm	0.394	0.491	0.281

Fines B- particles with diameter smaller than 10 µm and length above 0.2 mm as a percentage of total measured length.

Lc(l)- Length weighted length distribution of fibres

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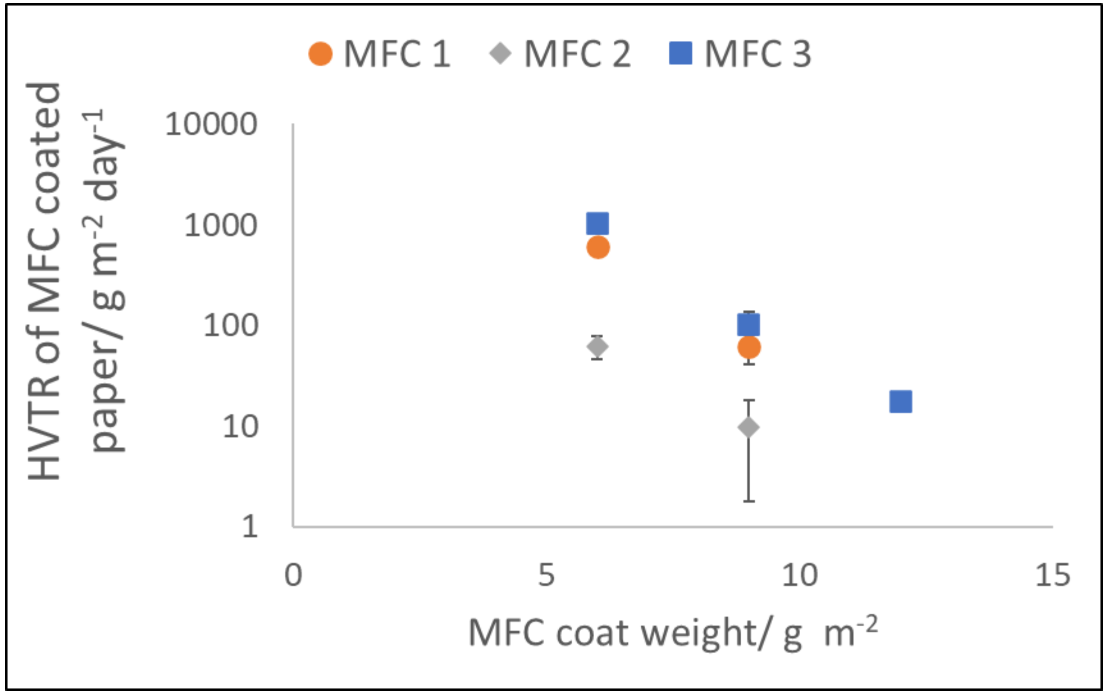
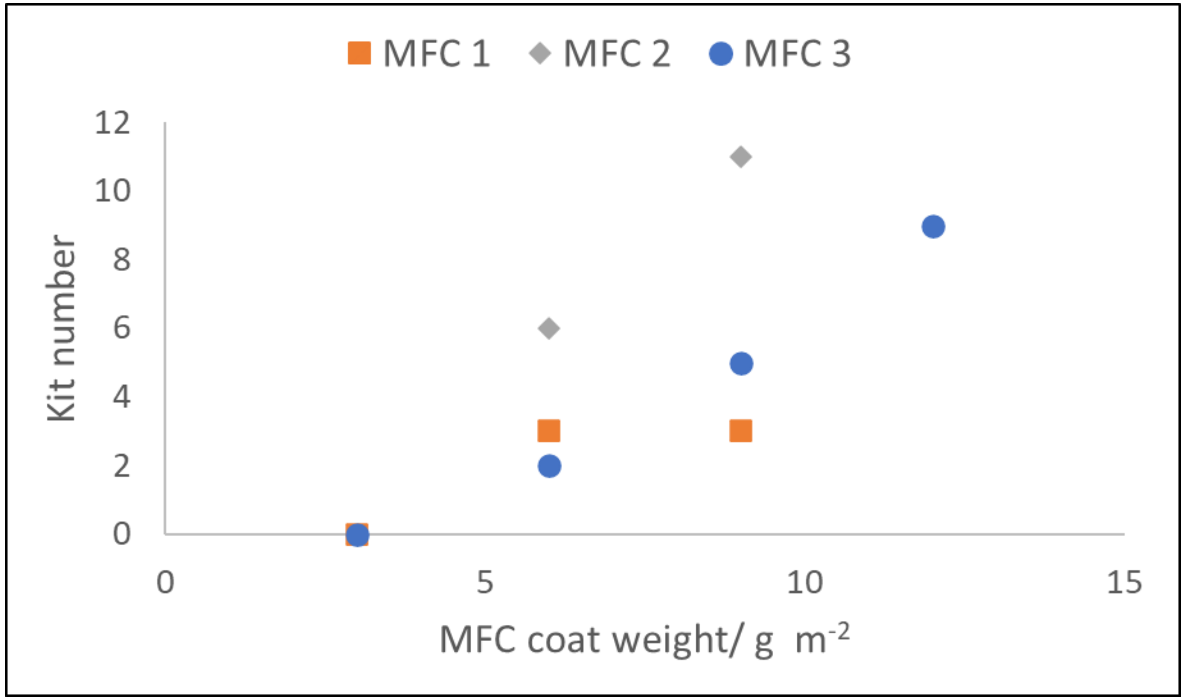
Valmet Fibre Image Analyzer- Owner's Manual K12690 V1.3, 2015

Can increasing coat weight make up for using a less fibrillated MFC? Part 2





- For MFC 1 and MFC 3, increasing coat weight was more effective than using a finer MFC sample.
- MFC 2 formed the most effective barrier layers.

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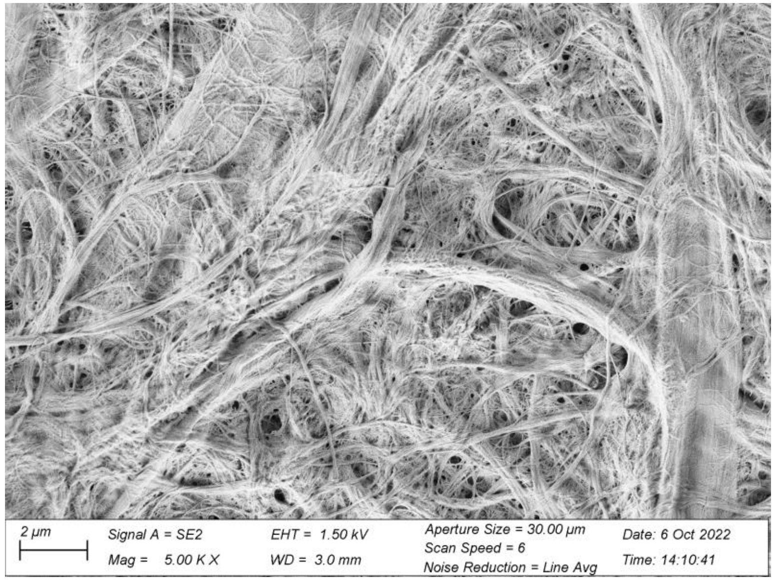
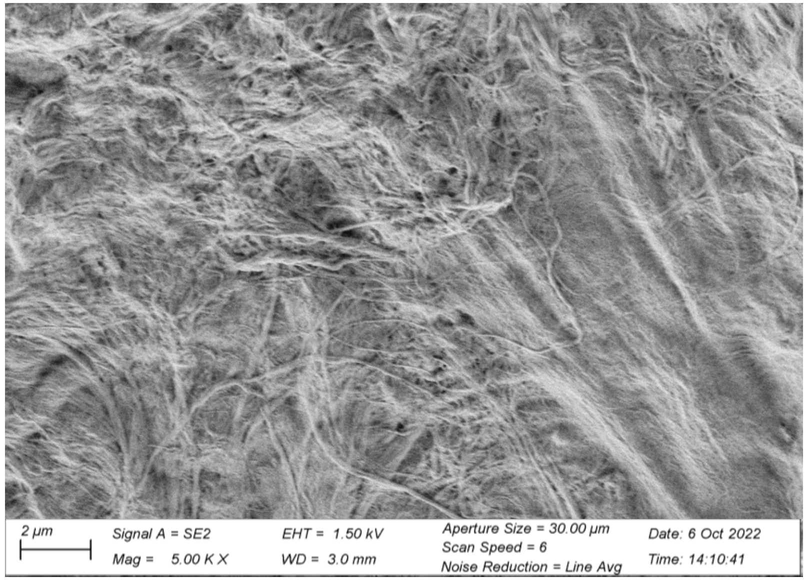
Why does the (apparently) less fibrillated sample have better barrier properties?

- MFC 1 had highest Fines B and highest tensile strength index of 20% MFC, 80% mineral sheets but performed less effectively than MFC 2.
- SEM images of dewatered MFC suspensions taken- no conclusive evidence either way.



MFC 1



MFC 2

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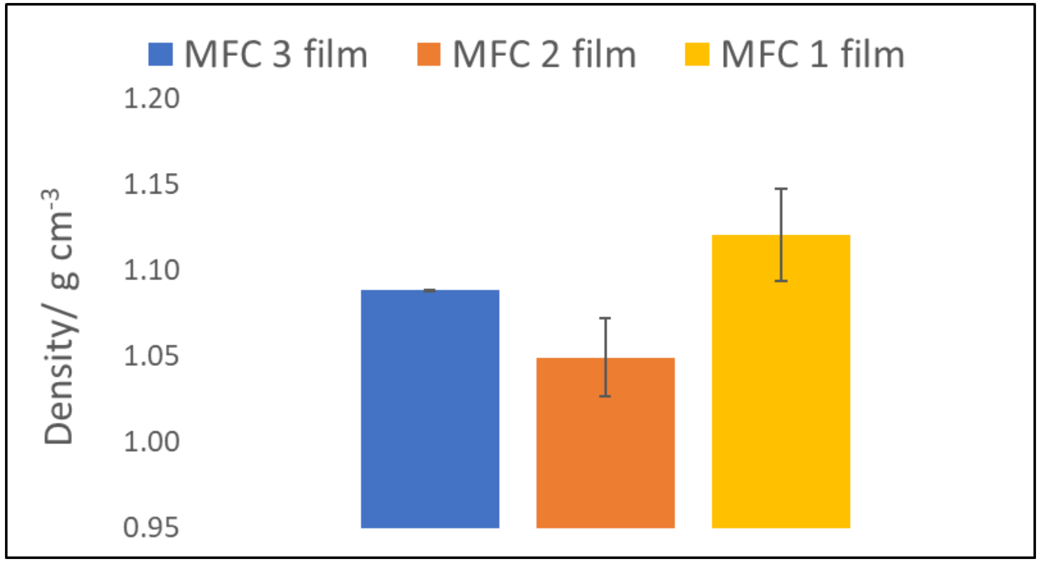
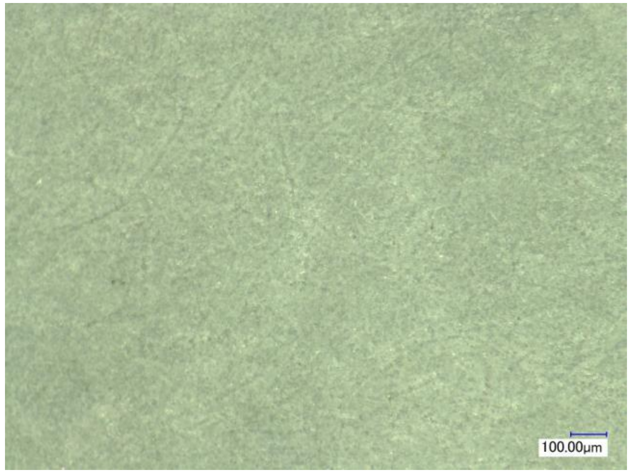
Can MFC films help explain differences between samples?

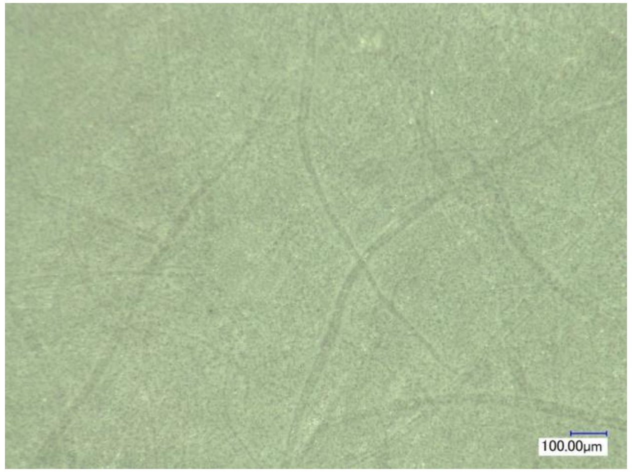
MFC 1 contained large fibre fragments- possibly these large fibres caused disruption in the MFC layer.



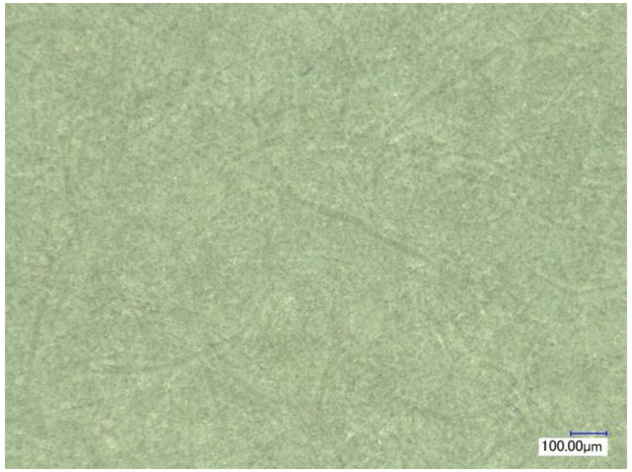
Density of MFC films showed that MFC 2 had the **lowest** density despite forming the most effective barrier coating layers.



Optical microscope image of MFC3 film



Optical microscope image of MFC1 film



Optical microscope image of MFC2 film

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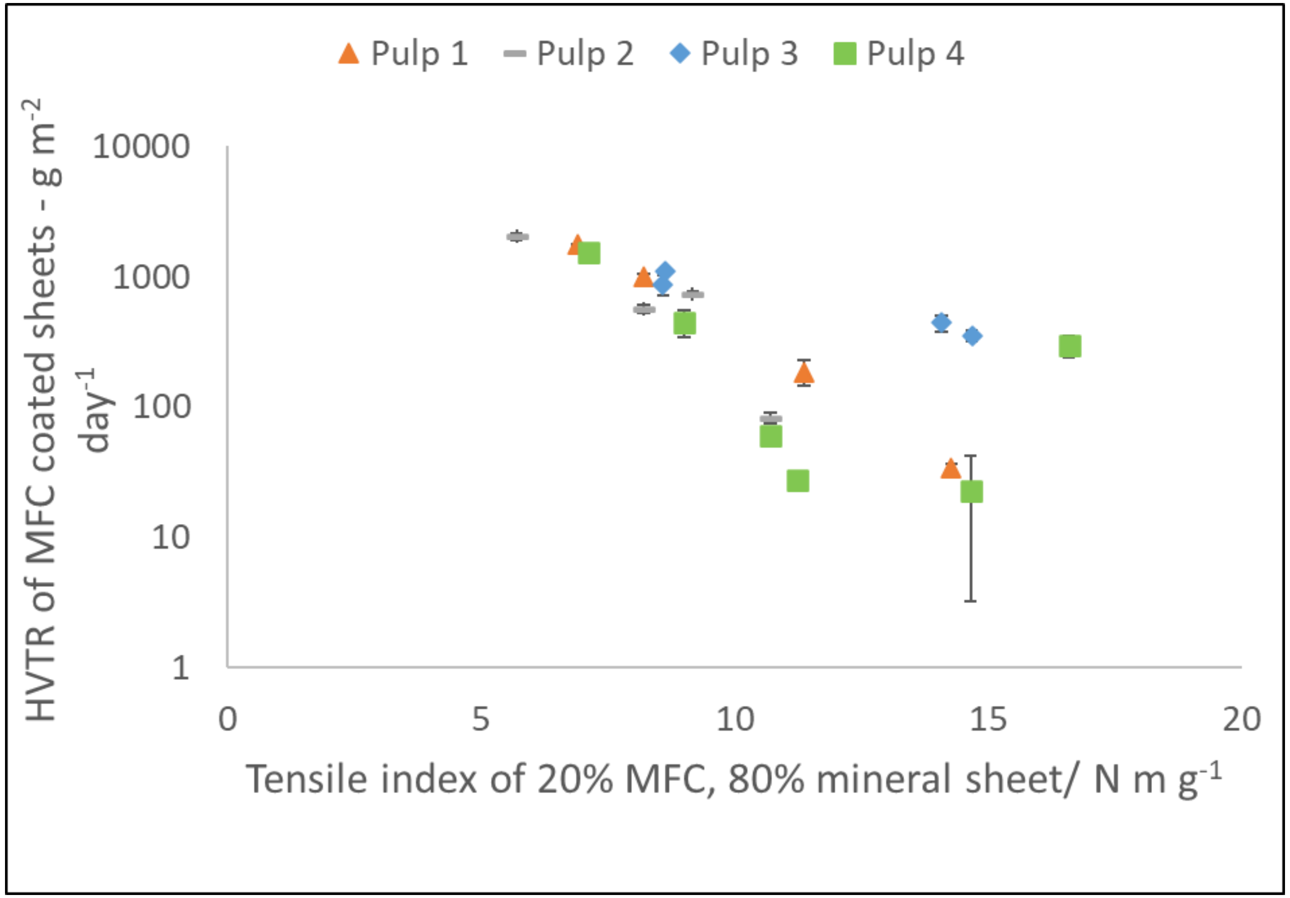
Can differences in pulp type explain different barrier properties?



- MFC samples were investigated from 4 pulp types.
- MFC samples coated at 6 g m^{-2} on base paper.
- For simplicity, samples are compared by the tensile index of MFC sheets made from 20% MFC and 80% mineral.
- MFC with a high proportion of fine material may be less effective at forming a continuous barrier film on the sheet surface.

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Conclusions

Increasing degree of fibrillation: Increasing fibre delamination improves barrier properties to heptane vapour and grease for MFC coatings.

Crystallinity: The Fiberlean MFC process may cause a small decrease in cellulose crystallinity index which could have contributed to a slight increase in WVTR for highly delaminated MFC samples.

Comparison of MFC samples

- MFC that appears to contain less fine material can be a more effective barrier layer.
  - Large fibre fragments in otherwise fine MFC samples may cause disruption
  - Changes in pulp type may have an effect
  - Very fine MFC materials may not form a continuous barrier film on porous base paper

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Thank you for your attention!

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