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The Effect of Microfibrillated Cellulose Characteristics on Barrier Properties for Packaging Applications

EngD Thesis

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Dedication

This thesis is dedicated to my family and friends for supporting me, and especially my dogs Lou and Rudi for always being there to cheer me up.

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Acronyms

FLT Fiberlean Tensile

HVTR Heptane vapour transmission rate

MFC Microfibrillated cellulose

NBSK Northern Bleached Softwood Kraft

RH relative humidity

WVTR water vapour transmission rate

XRD X-ray diffraction

Abstract

This thesis investigates how to most effectively use microfibrillated cellulose – a material made through separating cellulose fibres into smaller fibrils – as a barrier coating for packaging applications. Coating paper or cardboard with a layer of microfibrillated cellulose could provide a sustainable packaging solution since this provides a barrier layer to oxygen and grease. The research project began with looking into the thickness of the cellulose coating required to provide barrier properties and comparing two different base papers for the coating. Following this, the research project focused on how the extent of separation of cellulose fibres into fibrils affected the barrier properties of microfibrillated cellulose coatings, and whether there were cellulose characterisation methods which could help to predict whether a sample would have effective barrier properties. Therefore, the overall aim of the project was to determine how the characteristics of microfibrillated cellulose influenced the barrier properties when applied as a coating on paper or board. This knowledge would be useful to determine the process conditions required to make a microfibrillated cellulose which would provide optimised barrier properties when applied as a coating on an industrial scale. The chosen laboratory method for production of microfibrillated cellulose coated sheets was to use vacuum filtration to coat a layer of microfibrillated cellulose from a dilute aqueous suspension onto a commercial copy paper base sheet. This process aimed to replicate an industrial coating method used by Fiberlean Technologies. The sheets were then dried in paper driers to produce smooth, flat sheets. Barrier testing methods involved Kit testing to measure grease resistance, water vapour transmission rate, heptane vapour transmission rate and oxygen transmission rate. Optical properties of the microfibrillated cellulose films and coatings were also studied. The research showed that as the degree of fibrillation of cellulose increased from cellulose fibres to small fibril aggregates, the barrier properties of microfibrillated cellulose coatings to grease and heptane vapour improved. This relationship was still observed when microfibrillated cellulose from different pulp sources were used. However, when the extent of fibrillation further increased, there was a decrease in the barrier properties. This may be because the base sheet was porous and some fine cellulose may have been lost into the base sheet rather than remaining on the surface. This hypothesis was tested by applying MFC in multiple layers on the sheet surface. When a finer cellulose sample was applied as a pre-coating to a coarser cellulose sample, the barrier properties were less effective than when a coarser cellulose sample was applied as a pre-coat. This research project has determined that a microfibrillated cellulose with a medium level of separation of cellulose fibres into fibrils may be the optimum material to apply as a barrier coating on a porous paper or board substrate. This is because increasing the surface area of the cellulose through increasing mechanical treatment initially provides a significant increase in barrier properties, however, when the cellulose was comprised of mostly fine, liberated fibrils, the barrier properties decreased. Therefore, consideration of the pore structure of the base sheet relative to the size of the cellulose particles could be the most effective way to ensure that the optimum barrier properties are reached.

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Introduction

The introduction contains material published in a literature review written by the author which is included in the appendix.¹

Packaging is important to protect contents from damage. It also provides a barrier layer between the contents and the outside environment. The barrier layer can extend shelf life because the transport of gases such as oxygen and water vapour are reduced and leakage of water and oil is prevented. Single use plastics are common in packaging as they can have excellent barrier properties. However, many petroleum based plastics are not biodegradable.^{2,3} It is estimated that 275 million tonnes of plastic waste was produced in 2010, of which 12.5 million tonnes may have reached the world's oceans.⁴

More sustainable alternatives to non biodegradable, petroleum based plastics include polylactic acid (PLA), paper, or cardboard which are all biodegradable.^{2,5,6} However, PLA is classed as a low oxygen barrier when compared to other conventional plastics used in packaging.⁶ Paper and cardboard also have poor barrier properties due to their porous structure and are usually coated when used in food packaging.^{2,6}

For these sustainable packaging materials to be used in packaging, the barrier properties must be improved. Coating of paper or cardboard based material with polymers such as polyethylene, polypropylene or polyvinyl chloride is commonly used to provide a water vapour barrier. However, this makes the product difficult to recycle and non biodegradable.⁷ Paper or board is also often coated with per and poly fluoro alkyl substances (PFAS). Fluorine was found to be present in 46% of fast food wrappers or paper bags used in contact with food.⁸ PFAS molecules are thought to be able to migrate into food, are persistent in the environment, and human exposure to PFAS has been linked to health problems such as thyroid disease and some cancers.⁹ An alternative option which is thought to be more sustainable as the coated packaging can be recycled is the use of aqueous dispersions of polymer such as latex and mineral fillers as coatings for paper and board to improve the barrier properties.^{10,11} However, latex based coatings may not be biodegradable and may cause issues with plastic particles in paper recycling streams.^{11,12}

Applying a sustainable coating layer which provides good barrier properties to biodegradable polymers or paper and cardboard could help to improve the barrier properties and make a more sustainable packaging alternative.

A material, known as microfibrillated cellulose (Microfibrillated cellulose (MFC)), can be used to construct films or coatings with excellent oxygen barrier properties and water vapour barrier properties greater than that of cardboard or paper only.^{6,13} Section 1.2 describes the parameters used to compare the water and oxygen barrier properties of packaging materials and how the barrier properties of MFC films compare with commercial packaging materials.

1.1 | Cellulose and Microfibrillated Cellulose

Cellulose is a biopolymer comprised of glucose units joined by 1-4 glucosidic bonds. Cellulose molecules are arranged into elementary fibrils and held strongly by hydrogen bonds and Van der Waals forces. Elementary fibrils combine to form larger microfibrils which in turn assemble into cellulose fibres. Cellulose elementary and microfibrils have both crystalline and amorphous regions.¹³⁻¹⁷

Microfibrillated cellulose (MFC) was first produced by Turbak and co-authors and Herrick and co-authors by repeated mechanical treatment of a cellulose fibre slurry, resulting in a gel network of fibrils.^{18,19} MFC is described as the material made by applying mechanical force to cellulose fibres to split the larger fibre structure into microfibrils or microfibril aggregates. The fibrils also have a high aspect ratio, they are flexible and they contain both crystalline and amorphous regions. As a result of the smaller particle size, the surface area of MFC is comparatively much larger than the same mass of cellulose fibres. A chemical pre-treatment can be used to reduce the intensity of mechanical processing needed. The size distribution of the material depends on the production method and pre-treatments used.^{13,14,17,18,20}

An optical micrograph of cellulose fibres is shown alongside a Transmission Electron Microscope (TEM) image of MFC in Figure 1.1.²⁰ The change in morphology from a fibrous structure to a higher aspect ratio, higher surface area fibrillar structure is apparent between the cellulose fibres and MFC.

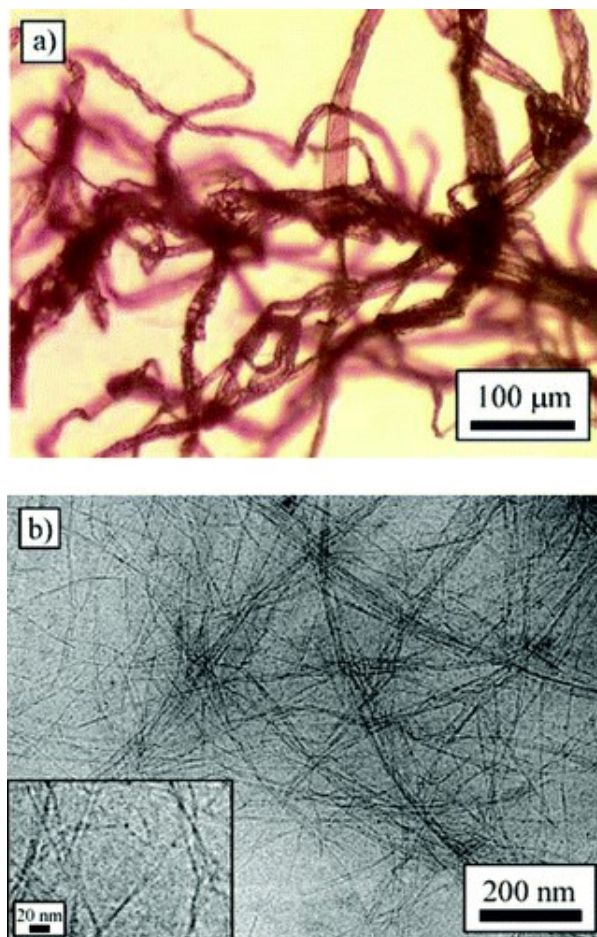


Fig. 1.1. Optical microscope image of cellulose fibres (a) and TEM image of MFC (b). Reprinted with permission from M. Pääkkö, M. Ankerfors, H. Kosonen, A. Nykänen, S. Ahola, M. Österberg, J. Ruokolainen, J. Laine, P. T. Larsson, O. Ikkala, and T. Lindström (2007), *Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels*, *Biomacromolecules*, 8(6):1934– 1941. Copyright 2007 American Chemical Society

Applying acid hydrolysis and mechanical treatment to cellulose fibres hydrolyses the amorphous regions of cellulose, producing cellulose nanocrystals (CNC).^{13,15} The difference in morphology between fibrillated cellulose materials and CNC is shown in Figure 1.2.²¹ Fibrillated cellulose, described here as a material produced through chemical or mechanical treatments on cellulose aiming to cause separation of fibrils from the main fibre, is sometimes also referred to as MFC, nanofibrillated cellulose (NFC), cellulose nanofibres or cellulose nanofibrils (CNF) in the literature.^{16,17,22–24} As discussed by Felipe Santos and co-authors, NFC is sometimes used to refer to finer size distributions than MFC, but the terms can also be used interchangeably.²⁵ For simplicity, these fibrillated cellulose materials will be referred to as MFC in this thesis. This thesis will focus on fibrillated cellulose materials which have been produced from cellulose fibres without an acid hydrolysis phase, therefore not considering the barrier properties of CNCs.

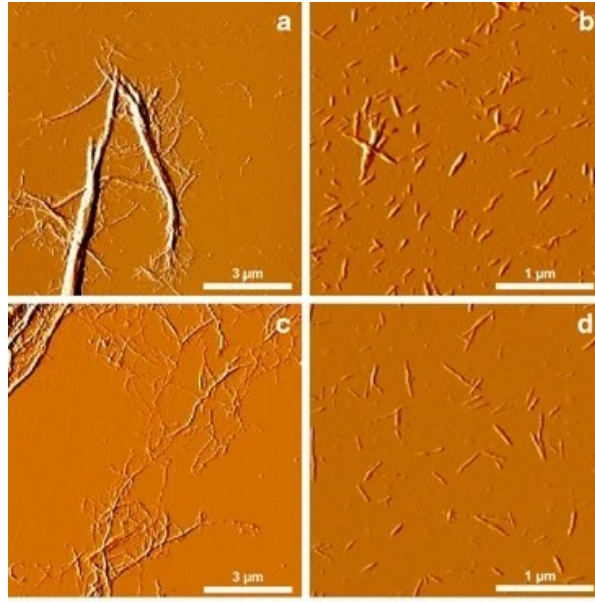


Fig. 1.2. AFM image of CNF before (a) and after (c) TEMPO mediated oxidation and CNC before (b) and after (d) TEMPO mediated oxidation (adapted) from: Substitution of nanoclay in high gas barrier films of cellulose nanofibrils with cellulose nanocrystals and thermal treatment, R. Bardet, C. Reverdy, N. Belgacem, I. Leirset, K. Syverud, M. Bardet and J. Bras, Cellulose, 22, 1227-1241, Springer Nature, 2015, reproduced with permission from Springer Nature. (Licensed material not part of governing OA license)

1.2 | Barrier Properties of Packaging

Oxygen transmission rate (OTR) and water vapour transmission rate (WVTR) describe the rate of oxygen or water vapour transmitted over time per sample area. Related parameters are oxygen permeability (OP) or water vapour permeability (WVP) which are calculated from the transmission rate using the sample thickness and the difference in vapour partial pressure on either side of the film. Equations 1.1-1.3 show how these parameters are calculated.⁶ Film thickness and vapour pressure are not always available in publications and therefore either transmission rate or permeability are used in this thesis, as reported by the authors.

$$WVTR \text{ or } OTR = \frac{\text{mass of water or volume of oxygen}}{\text{Area} * \text{time}} \quad (1.1)$$

$$WVP = \frac{WVTR * \text{thickness}}{\text{Saturated vapour pressure} * \Delta RH} \quad (1.2)$$

$$OP = \frac{OTR * \text{thickness}}{\text{change in oxygen partial pressure}} \quad (1.3)$$

Figure 1.3 shows the OTR and WVTR required for different food packaging applications.⁶ Both oxygen and water vapour barrier properties are commonly needed. Table 1.1 shows a comparison of the oxygen and water vapour barrier properties of an MFC film with single use plastics commonly used in food packaging. MFC shows low OP, comparable to poly vinylidene chloride or ethylene vinyl alcohol in dry conditions. However, the WVP of MFC films are high compared to other polymers. This limits the effectiveness of MFC in packaging requiring a

water vapour barrier. Furthermore, increasing humidity can lead to a significant decline in oxygen barrier properties of MFC, as discussed further in Section 2.3.1.²⁶ There have been attempts to improve the water vapour barrier properties of MFC through the addition of another biobased coating layer to provide the water vapour barrier, for example: beeswax or cooked starch;²⁷ shellac;²⁸ PLA;²⁹ or alkyd resin³⁰. Alternative strategies to improve the water vapour barrier properties of MFC are increasing the hydrophobicity of the cellulose,^{31,32} or adding platey minerals such as montmorillonite or bentonite.^{33,34}

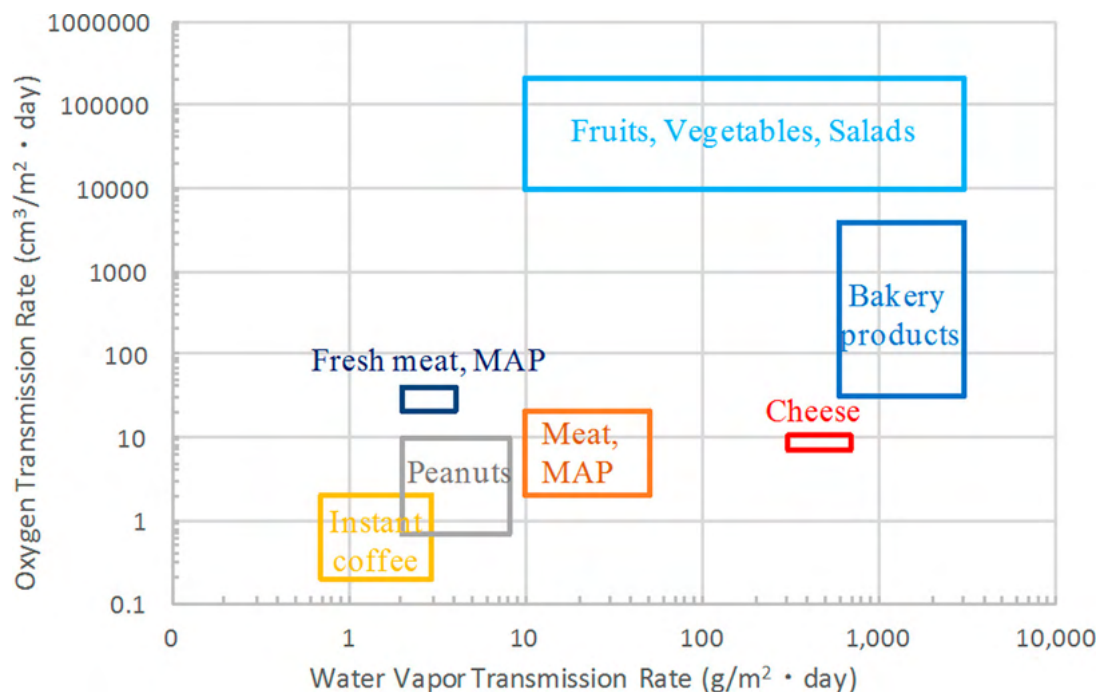


Fig. 1.3. Barrier properties required from different types of food packaging. Reprinted with permission from: J. Wang, D. J. Gardner, N. M. Stark, D. W. Bousfield, M. Tajvidi, and Z. Cai (2018) *Moisture and oxygen barrier properties of cellulose nanomaterial-based films*, ACS Sustainable Chemistry and Engineering 6(1):49–70, Copyright 2018 American Chemical Society

Table 1.1

Oxygen and Water Vapour Permeabilities of Polymers used in Food Packaging Compared to MFC

Material	OP $\text{cm}^3 \mu\text{m m}^{-2} \text{day}^{-1} \text{kPa}^{-1}$	WVP $\text{g} \mu\text{m m}^{-2} \text{day}^{-1} \text{kPa}^{-1}$
MFC Film	³⁵ 0.04 ± 0.008 @ 23°C, 50% RH	²³ 15700 ± 950 @ 23°C, 100% to 50% RH.
Polyethylene teraphthalate	³⁶ 10-50 @ 23°C, 50% RH	³⁷ 0.013 @ 21°C, 100% to 40% RH.
Polypropylene	³⁶ 500-1000 @ 23°C, 50% RH	³⁸ 493 ± 32 @ 37.8°C, 90% RH
Poly vinylidene chloride	³⁶ 0.1-3 @ 23°C, 50% RH	³⁹ 95 @ 23°C, 100% to 55% RH
Ethylene vinyl alcohol co-polymer	⁴⁰ 0.0223 ± 0.0002 @ 23°C, 0% RH	⁴⁰ 699 ± 76 @ 23°C, 95% RH
Poly lactic acid	⁴¹ 169 @ 23°C, 50% RH	⁴¹ 386 @ 23°C, 50% RH

1.3 | Aims and Objectives of the Project

The aim of this research was to understand how the process of increasing the separation of cellulose fibres into individual cellulose fibrils affects the barrier properties of MFC coatings. This involves gaining an understanding on how far along the process of separating fibres into fibrils we must be to achieve an MFC coating with excellent barrier properties. Furthermore, the project aimed to identify measurable characteristics of cellulose suspensions, films, or coatings which could act as screening tests to identify MFC samples that may form effective barrier layers. This is because the barrier testing methods described in Chapter 3 are time consuming, require specialised training, and require the use of hazardous solvents. A faster method to characterise and screen MFC samples would be an effective way to aid in selecting MFC samples that make effective barrier layers.

To achieve these goals, the research project first aimed to select a method to coat MFC onto base paper in the laboratory, and also identify how the coating thickness of the MFC layer influenced barrier properties of the coated paper. The next stage of the project was to apply a constant coat weight of MFC with an increasing degree of separation from fibres into fibrils, and measure the effect on barrier properties. Films of MFC were also made to measure the effect of increasing mechanical treatment on the crystallinity index of MFC films. Finally, the project looked into whether the relationship between fibrillation and barrier properties of MFC coatings applied across different pulp types. Characterisation techniques that could be used to screen out effective MFC samples were then investigated.

1.4 | Business case for the project

Fiberlean Technologies are a company that produces microfibrillated cellulose through a wet stirred media mill process. Fiberlean Technologies have developed an industrial method to

apply MFC as a coating onto paper and board at the wet end of a paper machine. This process is known as Fiberlean on Top and involves applying a jet of MFC suspension onto a wet paper web which has just been formed on the paper machine. Water is drained from the MFC suspension and wet paper web using the drainage system of the paper machine. After drying, this process results in a layer of MFC coated onto paper or board.^{42,43} Fiberlean Technologies were interested in using this coating technology to apply a barrier layer to paper or cardboard in order to expand into new markets since many examples of single use plastics are now being replaced with more sustainable alternatives.

When the present research project started, Fiberlean Technologies had completed some laboratory work on using cellulose as barrier coatings with favourable results.⁴³ This research project aimed produce an in depth investigation into the use of Fiberlean Technologies MFC as a coating for packaging where a barrier to air, oxygen, oil vapour or grease is required. For this technology to be successfully developed on an industrial scale, some fundamental knowledge of how to most effectively use the MFC to get the best barrier properties was required. For example, the effect of the thickness of the MFC layer on barrier properties was vital to understand to know how much MFC is required to be coated to form an effective barrier layer. Furthermore, MFC can be produced using a variety of energy levels and process conditions to produce cellulose with different levels of separation into individual cellulose fibrils. The extent of how fibrillated the cellulose is may be an important factor determining the barrier properties of the MFC. It is important to understand the level of fibrillation of cellulose required to produce barrier properties to understand the energy required in the cellulose fibrillation process and whether a process with lower energy could be used to produce the MFC.

Literature Review

The literature review contains material published in a literature review written by the author which is included in the appendix.¹

2.1 | Methods to Produce Microfibrillated Cellulose

Production of MFC usually involves a mechanical treatment such as homogenising, microfluidising, refining, or grinding with a Supermasscolloider. These can be coupled with enzyme or chemical treatments.^{13,44–47}

2.1.1 Enzyme Pre-treatments

To reduce the energy needed to produce MFC from cellulose and to prevent blocking of homogenisers, an enzyme pre-treatment can be used.^{13,20,48} Using enzymes rather than other chemical methods discussed later such as carboxymethylation and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) mediated oxidation may be more environmentally friendly since no hazardous reagents or solvents are required.^{49,50}

The hydrolysis of cellulose to glucose in nature uses enzymes known as cellulases. Endoglucanase enzymes are thought to break random glycosidic bonds within the cellulose fibrils in amorphous regions of the fibre, reducing overall chain length. Amorphous regions of cellulose are more common on the surface of the fibre and occur between crystalline regions of microfibrils. Therefore, the endoglucanase treatment swells the fibre walls, which leads to less energy being required to separate the fibrils during later processing stages.⁵¹ Cellobiohydrolases then act from the ends of cellulose molecular chains and hydrolyse cellulose into smaller, soluble derivatives. Glucosidase then breaks down these soluble cellulose derivatives into glucose.^{48,51,52}

2.1.2 Deep Eutectic Solvents

A deep eutectic solvent refers to a mixture of materials where the melting point of the mixture is lower than any individual component as a result of strong hydrogen bonding.⁵³ MFC was produced by heating cellulose pulp in a mixture of choline chloride and urea which forms a deep eutectic solvent prior to passing through a microfluidiser by Sirviö and co-authors.⁵³ The deep eutectic solvent treatment allowed the pulp to pass through the microfluidiser without clogging which was not possible for untreated pulp. Li and co workers found that pre-treatment of cellulose fibres with deep eutectic solvents resulted in an increase in fibre width which suggested that the fibres were swelling.⁵⁴

2.1.3 Chemical Pre-treatments

Using a chemical pre-treatment before mechanical processing can help to separate cellulose into individual nano sized fibrils.⁵⁵ For a comprehensive review of chemical pre-treatments

used on cellulose prior to fibrillation, readers could refer to the review by Nechyporchuk and co-authors.⁴⁵

2.2 | Characterisation of Microfibrillated Cellulose

This review focuses on how different cellulose pre-treatments and MFC production methods affect the barrier properties of MFC films and coatings. Therefore, it is important to characterise the MFC so as to understand the effects of the size distribution and morphology of cellulose on barrier properties. The same methods of MFC characterisation are not used in every study discussed in the present review, making direct comparisons about MFC characteristics and barrier properties across different publications difficult. For detailed discussion of characterisation of MFC, the reader is referred to Kangas and co-authors²² or Osong and co-authors⁵⁶. For a specific discussion on characterising the crystallinity of cellulose, the reader is referred to Park and co-workers⁵⁷.

Table 2.1 shows a summary of the advantages and disadvantages of different characterisation methods used by studies discussed in this review. Indirect methods of characterisation, for example viscosity of suspensions or light scattering provide, less detailed information than imaging methods but have the advantage of providing a fast, quantitative comparison of samples.²²

2.3 | Barrier Properties of Microfibrillated Cellulose

Gases are thought to travel through polymer films via dissolution in the polymer matrix, diffusion across a concentration gradient, and evaporation on the other side of the film. The transport through the polymer therefore depends on the solubility of the gas and how easy it is for the molecules to travel through the polymer matrix. The solubility of a gas through a polymer depends on chemical interactions between the gas and functional groups of the polymer. However, strong interactions between polymer chains can slow diffusion since the chains are held closely and mobility is restricted. Increasing crystallinity of the polymer decreases diffusivity because crystalline regions are impermeable and increasing the fraction present increases the path length for diffusing gases. Crystalline regions further restrict transport because they reduce the mobility of surrounding amorphous polymer chains, leading to decreased free volume within the polymer.⁶⁶ Comparing an MFC film or coating to a polymer film, it appears that factors such as changing the physical structure and porosity of the MFC film, altering the crystallinity of the cellulose, and altering the chemical properties of the cellulose would all have an influence on barrier properties of the film.

With regards to the physical structure of an MFC film, Syverud and Stenius found that MFC films have a low air permeability and suggested that this meant there were no connecting pore channels running from one side of the MFC film to the other.⁶⁷ Aulin and co-authors measured the density of films made from MFC produced by carboxymethylation followed by microfluidization as $1.57 \pm 0.03 \text{ g cm}^{-3}$. The authors argued that the film density was between the densities of crystalline and amorphous cellulose, therefore, implying that porosity within the films is low and that there is little pore space for diffusing gases to travel through.²⁶ SEM images of MFC film surfaces and cross sections shown by Aulin and co-authors and Minelli and co-authors show that there is surface porosity between fibrils but a dense layered middle structure.^{26,68} An example is shown in Figure 2.1²⁶. The work of Aulin and co-authors, Minelli and co-authors, and Syverud and Stenius suggests that the physical structure and porosity of the MFC film is one of the key reasons for the excellent barrier properties.^{26,67,68} This suggests

Table 2.1

Overview of MFC characterisation methods used in studies discussed in this review

Method	Advantages	Disadvantages
Fibre image analyser	Provides a quantitative description of MFC, allowing comparison between samples.	Some fibrils are too small to be detected by fibre image analysers which work through optical imaging. ⁵⁸
Microscopy: Optical, SEM, TEM or AFM	A useful tool for understanding morphology of the material. ²²	Requires extensive time to image representative samples. ⁵⁶
X-ray diffraction	Measures a crystallinity index of cellulose which can be used to compare samples. ⁵⁷	The commonly used peak height determination of crystallinity index may not give a true quantitative value. ⁵⁷
Mass percentage remaining in supernatant after centrifuging	Quantitative measurement of mass percentage of fine material which can be used to compare samples. ⁵⁹	No structural information about material remaining in the supernatant. ²²
Viscosity of MFC suspensions	Increasing separation of fibres into fibrils can be estimated by increasing suspension viscosity. ⁶⁰	Fibril length can be an important factor in measured viscosity so it is not always clear if a lower viscosity is due to lower fibrillation or reduced fibril length. ²²
Light transmittance of MFC suspensions	Quantitative comparison between samples since cellulose samples that are more fully dispersed into fibrils have higher transmittance. ⁶¹	If the particle diameter approaches the light wavelength, scattering can increase which results in a lower transmittance. ²²
Specific surface area through Congo red dye absorption	Quantitative comparison of surface area between cellulose samples. ⁶²	Absorption of Congo red dye can be affected by crystallinity and lignin content of cellulose which may affect results. ^{62,63}
Degree of polymerisation	Degree of polymerisation measurement compares the length of the cellulose chains or the degradation of the cellulose molecular structure. ^{22,64}	Degree of polymerisation can give an estimate of fibril length but the true value can be greater than cellulose chain length suggests. ⁶⁵

that changing the physical structure of the cellulose by increasing separation of fibrils from fibres may lead to improvements in barrier properties of MFC films.

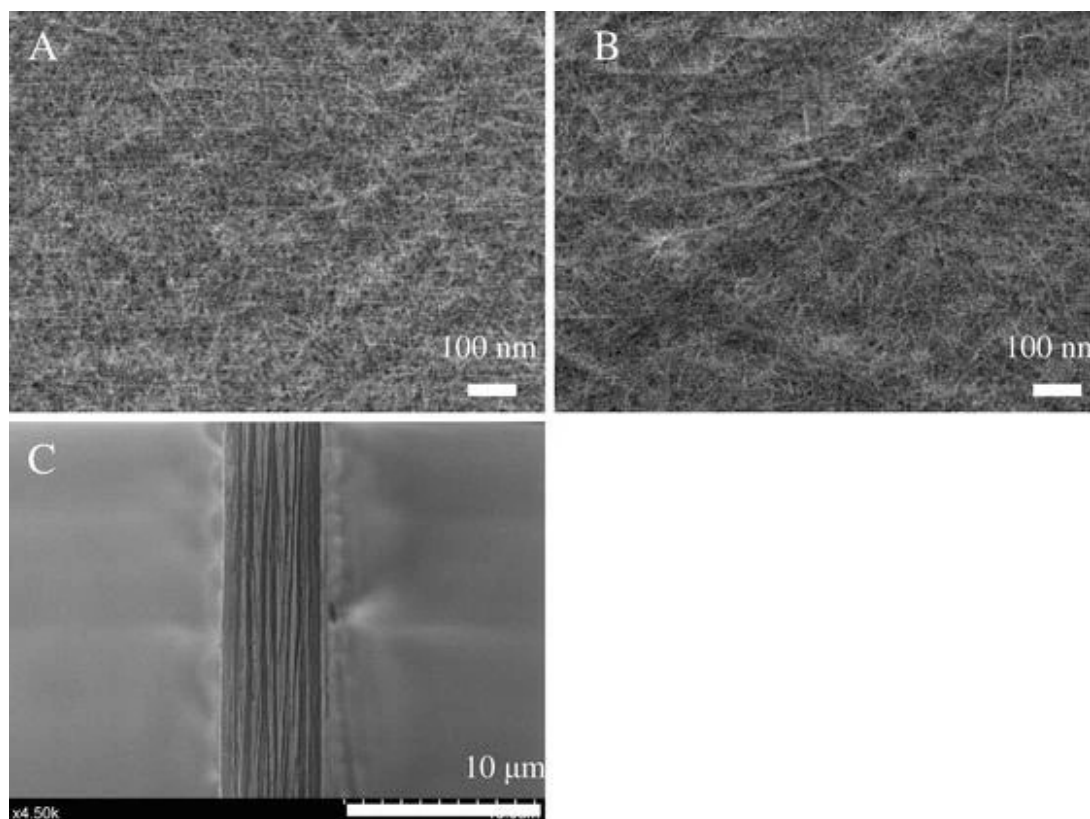


Fig. 2.1. SEM images of surface (A,B) and cross section (C), of MFC films. Reprinted from: *Oxygen and oil barrier properties of microfibrillated cellulose films and coatings*, C. Aulin, M. Gallstedt, T. Lindstrom, *Cellulose* 17(3):559– 574, 2010, reproduced with permission from SNCC. (Licensed material not part of governing OA license)

The porosity of MFC films has been studied using Positron Annihilation Lifetime Spectroscopy (PALS). For example, Fukuzumi and co-workers used PALS to measure the averaged pore size of MFC films made from TEMPO oxidised cellulose— which was 0.47 nm at 0% relative humidity (RH)— and these pores did not connect throughout the film.⁶⁹ Roilo and co-authors also used PALS to study the pore size of TEMPO oxidised MFC films and found that the size of pores, in this paper described as diameters of long spaces between fibrils, was approximately 0.31 nm (RH not provided).⁷⁰ Torstensen and co-authors also used PALS to characterise TEMPO oxidised cellulose films but in contrast to the publications above described the pores as spaces between amorphous cellulose chains rather than between cellulose fibrils. This value was 0.215 nm at 0% RH.⁷¹ In contrast, Orsolini and co-workers measured the average pore diameter of MFC films through mercury intrusion porosimetry as 28.6 ± 2.3 nm.⁷² However, Orsolini and co-workers used MFC produced through mechanical only processing to form the films without the TEMPO mediated oxidation step, leading to a material with fibril diameters below 100 nm.⁷² In contrast, Roilo and co-workers measured average fibril diameter as 4 nm, showing a significant fibril diameter size difference between the two types of materials which may account for the significant difference in measured pore size.⁷⁰

Roilo and co-authors further studied the influence of pore size on permeability by measuring the transport of hydrogen gas and helium gas as well as nitrogen and carbon dioxide. No transmission of carbon dioxide or nitrogen gas could be measured but permeability of $\text{He}_{(g)}$ and $^2\text{H}_{2(g)}$ were 0.4 ± 0.1 and 0.1 ± 0.03 mL $\mu\text{m m}^{-2} \text{ day}^{-1} \text{ kPa}^{-1}$ respectively. The kinetic

diameters of $\text{He}_{(g)}$ and $^2\text{H}_{2(g)}$ are 0.26 and 0.289 nm whereas CO_2 and N_2 have kinetic diameters of 0.364 nm and 0.33 nm.⁷⁰ The authors concluded that helium and deuterium gas were able to pass through the MFC layer because their kinetic diameters were smaller than the size of the pores but larger gas molecules could not pass through at a rate high enough to be measured.⁷⁰ This experiment could explain why MFC films made from finely dispersed cellulose fibrils such as those made through TEMPO mediated oxidation show excellent oxygen barrier properties. The oxygen molecules may be too large to travel through elongated channels between fibrils as proposed by Roilo and co-authors.⁷⁰ However, MFC made from coarser or more polydisperse material is likely to form films with a higher degree of physical porosity and therefore allow the transport of oxygen. In this case, the mechanism for the oxygen barrier may be the lack of connecting porosity as suggested by Aulin and co-authors, Minelli and co-authors, and Syverud and Stenius.^{26,67,68}

Aulin and co-authors and Syverud and Stenius suggested that the crystalline regions of cellulose may help to improve the barrier properties of MFC films.^{26,67} However, Belbekhouche and co-workers found that films of MFC had lower oxygen permeability than films made from CNC despite the CNC having a higher crystallinity. The authors suggested this could be partly due to chemical differences between the materials, but also because the MFC forms a more entangled, dense network with little connecting porosity which is more effective in inhibiting gas diffusion.⁷³

2.3.1 The Effect of Water on MFC Barrier Properties

MFC films can be good barriers to oxygen at low RH but, at high RH, the oxygen permeability increases. MFC is a hydrophilic material due to many accessible hydroxyl groups on the fibril surfaces which leads to water sorption at high humidity as a result of a favourable decrease in free energy.^{26,68,74} This water sorption reduces the hydrogen bonding between fibrils and allows swelling of the films which may then provide more open porosity allowing for oxygen diffusion.²⁶ The increase in oxygen permeability at high RH is observed also for ethylene vinyl alcohol (EVOH) due to an interruption in hydrogen bonding by water molecules.⁶⁶ Torstensen and co-authors used PALS to measure the size of free volume holes within TEMPO oxidised cellulose films. Upon increasing relative humidity, there was an initial decrease in the size of free volume holes, followed by an increase. This led to the explanation from the authors that initially at low RH, water binds between cellulose molecules and as the RH further increases, the pores swell which pushes chains apart and eventually leads to increased porosity within the film.⁷¹ A swelling of the amorphous regions of cellulose resulting in a porous structure upon exposure to moisture was also observed by Garg and co-authors.⁷⁵ Further evidence for swelling leading to increasing oxygen transmission at increased relative humidity was seen by Miettinen and co-authors who found that the thickness of an MFC film, measured through X-ray microtomography, increased as the relative humidity increased.⁷⁶

The deterioration in oxygen barrier at high RH is a significant issue which needs to be considered when replacing other barrier materials with MFC. Numerous studies have used hydrophobization of MFC in order to reduce the water vapour transmission rate of the material or to reduce the oxygen transmission rate at high relative humidity.^{31,32,77–79}

2.4 | The Effect of Pre-treatment and Process Conditions on the Barrier Properties of MFC

2.4.1 Increasing Mechanical Processing

Increasing the Intensity of one Fibrillation Method with no Chemical Pre-treatment

Publications studying the effect of increasing mechanical treatment without any chemical pre-treatment to help facilitate fibrillation are summarised in Table 2.2.

Table 2.2

Summary of previous studies on the effect of increasing intensity of mechanical treatment on barrier properties of MFC films or coatings without a chemical pre-treatment stage

Reference	MFC production	Findings
⁵⁸	Grinding using Supermass-colloider	Increasing number of passes decreased OTR.
⁸⁰	Grinding using Supermass-colloider	Increasing number of passes decreased WVTR but effect plateaued.
⁸¹	Grinding using Supermass-colloider	At low film grammage, increasing number of passes decreased OTR.
⁸²	Increasing number of passes through refiner	Increasing number of passes decreased OTR and hexane vapour transmission.
⁸³	Increasing number of passes through microfluidiser after a Supermasscolloider grinding stage.	WVP decreased at 50% RH for MFC films, no effect measured for OP.

Padberg and co-workers compared the OTR of MFC cast films where the MFC was passed through a Supermasscolloider grinder an increasing number of times. The study found that the films produced from MFC made using ten passes through the grinder presented excellent oxygen barriers beyond the sensitivity of the test whereas the films produced from MFC made from nine passes were poor oxygen barriers. This effect was linked to the increased %Fines content and decreased large fibre fragments in the MFC observed in the fibre analyser data. Furthermore, mercury porosimetry analysis showed a decrease in pore volume in MFC films between 9 and 10 grinder passes.⁵⁸ In a similar study, Nair and co-workers studied the effect of increasing number of passes on the water vapour permeability of MFC films and found that initially, there was a significant decrease in water vapour permeability as the number of passes through the grinder increased but after 3 passes a plateau was reached.⁸⁰ Also looking into increasing the degree of fibrillation by passing cellulose fibres through a Supermasscolloider grinder with increasing number of passes, Bessonoff and co-authors found that for low film thicknesses, increasing number of passes from 4 to 9 decreased OP. However, the OP difference between the samples significantly decreased as the film thickness increased, suggesting that film thickness affects the influence of fibrillation on barrier properties of MFC films.⁸¹ By passing cellulose fibres through a disc refiner an increasing number of times to make increasingly fine MFC, Juntunen found that increasing the number of passes decreased the hexane vapour transmission rate of MFC coated onto filter paper. Similarly, there was an

abrupt and significant reduction in oxygen transmission rate. This decrease in hexane vapour transmission rate corresponded with an increase in MFC suspension viscosity, suggesting that the higher degree of separation of the cellulose into fibrils was the reason for the decreasing hexane vapour transmission rate.⁸² This trend is similar to the findings of Padberg and co-authors⁵⁸ and implies that the development of barrier properties occurs once the cellulose is sufficiently delaminated that it forms networks with no connecting porosity.

In a similar study to Juntunen, Nair and co-workers and Padberg and co-authors^{58,80,82}, Wei and co-authors investigated how increasing the number of passes of Supermasscolloider ground MFC through a microfluidiser affected the barrier properties of MFC films. The study found that at 50% RH, increasing the number of passes through the microfluidiser decreased WVP of the films, supported by an increase in density of films as number of passes increased. However, when accounting for variation there was no significant decrease in WVP at 90% RH or OP at 50% or 90% RH.⁸³

Both Padberg and co-authors⁵⁸ and Wei and co-authors⁸³ investigated the effects of changes in cellulose crystallinity through mechanical processing since crystallinity is thought to be an important factor in the barrier properties of polymers. Wei and co-authors measured crystallinity of the MFC films through Raman spectroscopy and found that crystallinity index decreased as the number of passes through the microfluidiser increased. The authors suggested that this decrease in crystallinity did not have a negative effect on the water vapour barrier properties of the films and that the increasing density of the film resulting from finer fibrils had a larger impact on the barrier properties than decreasing the crystallinity.⁸³ Similarly, Padberg and co-workers measured crystallinity of MFC films through X-ray diffraction and found that the crystallinity index decreased when increasing number of passes through the Supermasscolloider grinder were used. However, a detrimental effect on the OTR was not seen and therefore it was assumed that the changes in physical structure of the film from increasing cellulose fibrillation had a greater impact on the oxygen barrier properties than decreasing cellulose crystallinity.⁵⁸

Addressing the effect of larger cellulose fibre fragments on oxygen barrier properties, Herrera and co-authors compared the oxygen transmission rates of films produced from MFC produced via TEMPO mediated oxidation followed by microfluidization with and without removing larger cellulose particles via centrifugation. The authors found that films made from the unfractionated samples had a higher OTR at 30% and 50% RH than the films made from the fractionated samples. This suggests that large fragments may have a disruptive effect on MFC film barrier properties.⁸⁴ This could explain why the effect of increasing fibrillation on MFC barrier properties appears to plateau- once large fibres are removed, a dense network can form with low connecting porosity.

A review article by Naderi and Lindström suggested that increasing separation of cellulose fibres into fibrils has an initial effect in improving barrier properties of MFC films, but once a very fine material is reached, there is no further benefit in increasing the mechanical treatment intensity.⁸⁵ This idea is supported by the results of Nair and co-authors, Padberg and co-authors and Wei and co-authors.^{58,80,83} The work of Bessonof and co-authors suggests that the film thickness may play a role in the threshold degree of fibrillation required to form optimum barrier properties.⁸¹ Furthermore, Roilo and co-authors suggested that the method of transport through MFC depends on the pore size within the material and gases can diffuse through the pore space if the pores are large enough.⁷⁰ Therefore, if the degree of fibrillation is high enough to prevent gas travelling through pore space, there is no further benefit to increasing fibrillation. Chinga-Carrasco and Syverud found that increased density of MFC films led to decreased OTR which supports the theory that decreasing pore space is beneficial as denser films have less pore space.⁸⁶

Results from Nair and co-authors⁸⁰ and Padberg and co-authors⁵⁸ appear to support the hypothesis that initially increasing the fibrillation of cellulose improves gas barrier properties, but this effect does not continue as the fibrillation increases. This could provide valuable insight into the mechanism of the gas barrier of MFC films. As described in Section 2.3, Aulin and co-authors,²⁶ Minelli and co-authors,⁶⁸ and Syverud and Stenius⁶⁷ suggest MFC forms barrier layers because there is no connecting porosity through the MFC layer. Therefore, it could be the case that for coarse MFC with large fibre fragments and few very fine fibrils, there remains some connecting porosity within the layer which allows the diffusion of gases. As the degree of fibrillation increases, the tortuosity of the diffusion pathway increases, increasing the path length and reducing the number of possible routes. Eventually there is no remaining connecting porosity in the MFC layer and as such a plateau in gas barrier properties is reached. This implies that any remaining diffusion through the MFC film may be taking place through a different mechanism.

Furthermore, the examples of Nair and co-authors⁸⁰ and Padberg and co-authors⁵⁸ highlight an important difference between the oxygen and water vapour barrier properties of MFC films. While Padberg and co-authors⁵⁸ found that increasing the fibrillation led to no detectable transmission of oxygen, Nair and co-authors⁸⁰ found that there was a plateau in water vapour permeability as the extent of disintegration of the cellulose fibres increased. This plateau value of water vapour permeability seen by Nair and co-authors⁸⁰ could mean there was no remaining connecting porosity within the film for the water vapour to diffuse through and the constant water vapour permeability could have been the amount of water that could sorb through the amorphous regions of cellulose fibres as explained by Belbekhouche⁷³ and co-authors and Okubayashi and co-authors⁸⁷.

The Effect of Different Mechanical Treatments

A summary of investigations into how different mechanical treatments, without a chemical pre-treatment, affect the barrier properties of MFC films and coatings is shown in Table 2.3. The studies of Hasan and co-authors²³ and Kumar and co-authors⁸⁸ both compared the oxygen and water vapour barrier properties of films made from MFC produced by refining only and MFC produced with an additional Supermasscolloider grinding step. Kumar and co-authors found that the additional grinding stage did not decrease oxygen or water vapour transmission rates of MFC films when accounting for standard deviation within the results.⁸⁸ However, Hasan and co-authors reported a statistically significant decrease in OP and WVP when using the MFC from the additional grinding stage compared to refining only.²³ Kumar and co-authors found that the MFC produced by refining with a grinding stage had more fine fibrils visible in SEM images than MFC produced by refining only.⁸⁸ Similarly, Hasan and co-authors measured smaller fibril diameters for the ground MFC and a narrower fibre distribution.²³ The difference in results could be explained by the fact that the two studies used different pulp types which may have different relationships between fibrillation and barrier properties.

Similarly, Spence and co-authors (2011) found that a refining treatment significantly reduced WVTR of films compared to untreated pulp only and that a further decrease in WVTR was observed after an additional grinding treatment with a Supermasscolloider or a homogenizing treatment. The WVTR of a sample produced through grinding with a Supermasscolloider only was also measured and it was higher than that of the sample made with a refining pre-treatment.⁶³ In agreement with these conclusions, Spence and co-workers (2010) investigated the effect of a refining pre-treatment followed by homogenization on different pulp samples. The study found that WVTR of films produced from the samples decreased significantly after refining compared to the pulp only and decreased further after the homogenization treatment.⁸⁹

Table 2.3

Findings from literature studies on the effect of increasing mechanical treatment on barrier properties after a chemical pre-treatment

Reference	MFC production	Findings
63	MFC produced through different mechanical treatments.	Refining decreased WVTR of MFC compared to pulp only. Additional mechanical treatment stages have different effects on WVTR.
23	Refining or refining followed by grinding using Supermass-colloider.	Decrease in OP and WVP after additional grinding stage compared to refining only.
88	Refining or refining followed by grinding with Supermass-colloider.	Small decrease in WVTR and OTR with additional grinding stage but not larger than variation in results.
89	Refining or refining followed by homogenizing.	Refining effective in reducing WVTR compared to pulp. Extra homogenizing stage only decreased WVTR for some pulp types.
90	Refining followed by twin screw extrusion, homogenization or grinding.	Little difference in WVTR or OTR, when accounting for variation, between MFC production methods.

The studies of Spence and co-authors (2010)⁸⁹ and Spence and co-authors (2011)⁶³ both use the absorption of Congo red dye as a measure of the specific surface area of MFC. This method was performed by adding Congo red dye into MFC suspensions, and centrifuging after incubation. UV-vis spectroscopy was then used to calculate the concentration of dye in the supernatant and therefore the amount of dye that had adsorbed onto the cellulose.⁸⁹ This quantitative measure of degree of fibrillation was used to plot the WVTR/thickness measurements given in both papers against the specific surface area of the MFC in Figure 2.2. A general trend of increasing surface area leading to decreasing WVTR before appearing to reach a plateau is shown in the graph. This agrees with the results from Nair and co-authors which show a similar trend of increasing fibrillation leading to decreased WVTR then reaching a plateau.⁸⁰

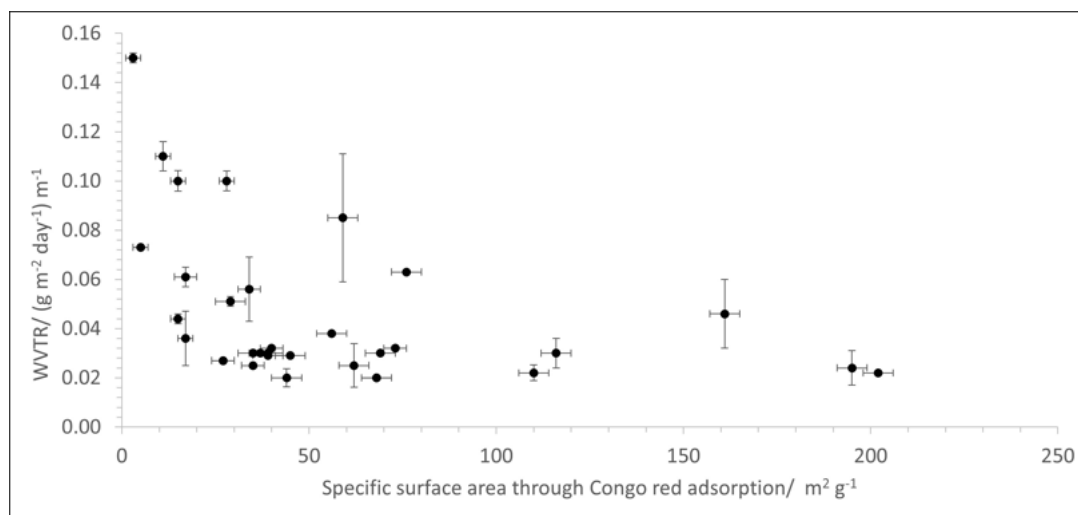


Fig. 2.2. Graph of WVTR/ thickness as a function of the specific surface area of MFC measured through the absorption of Congo red dye. Graph compiled from data from⁸⁹ and⁶³. Error bars refer to standard deviations given in the papers.

Spence and co-authors (2011) found that specific surface area of fibrils measured through absorption of Congo red dye significantly increased after the refining pre-treatment and further increased after grinding. However, the sample produced through grinding only had a higher surface area than that made with a refining pre-treatment which suggests higher fibrillation but also presented a higher WVTR.⁶³ It is possible that this high surface area was due to more very fine fibrils being present, but there may still have been some large fibre fragments which caused disruption in the film and increased WVTR. The authors also found that microfluidization post refining did not lead to a decrease in WVTR for bleached pulp, despite increasing specific surface area of the MFC. For unbleached pulp samples, microfluidization did produce a decrease in WVTR, but the WVTR values were higher than the bleached pulp to begin with.⁶³ This highlights that multiple factors including chemical differences between pulp types can affect how barrier properties of MFC vary with fibrillation.

Espinosa and co-authors compared different mechanical treatments to produce MFC after refining pulp. The authors found that the percentage of nanofraction of pulp measured through centrifugation was lower for both the unbleached and bleached pulp produced through twin screw extrusion than homogenization or grinding. The MFC produced through homogenization had the lowest fibril diameter in both bleached and unbleached pulps. However, when accounting for variation there was little difference between OTR values for the MFC produced through different processes.⁹⁰ This result highlights that finding a measurement to explain and predict barrier properties of MFC is elusive due to difficulty in characterising the material.²²

Increasing Intensity of Mechanical Fibrillation after a Chemical Pre-treatment

A summary of six studies investigating the effect of increasing mechanical processing on the barrier properties of MFC films or coatings after a chemical pre-treatment on the fibres designed to enhance fibrillation is shown in Table 2.4.

Table 2.4

Findings from literature studies on the effect of increasing mechanical treatment on barrier properties after a chemical pre-treatment

Reference	MFC production	Findings
26	Carboxymethylation followed by homogenizing.	Increasing passes through homogeniser did not decrease OTR.
91	Carboxymethylation followed by homogenizing.	Increasing number of passes did not decrease OP.
92	Grafting CMC followed by microfluidizing.	Increasing number of passes decreased OP.
88	TEMPO mediated oxidation followed by homogenizing.	Increasing number of passes did not decrease OTR.
93	TEMPO mediated oxidation followed by homogenizing and sonicating.	Increasing mechanical treatment intensity increased OTR and did not affect WVTR.
94	Phosphorylation followed by microfluidizing.	Increasing number of passes had different effects depending on degree of substitution and relative humidity of testing environment.

Aulin and co-authors^{[26](#)} and Siró and co-authors^{[91](#)} used a carboxymethylation pre-treatment and subsequently measured oxygen transmission rate or oxygen permeability of MFC films made through increasing number of passes through a microfluidiser or homogeniser. Neither study found a significant improvement in oxygen barrier properties with increasing numbers of passes through the homogeniser or microfluidiser despite the presence of fewer large fibre aggregates in both cases. For example, Aulin and co-authors found no significant decrease in OTR between 1 and 10 passes through the microfluidiser.^{[26](#)} Similarly, Siró and co-authors found no significant decrease in OP when the number of passes of carboxymethylated cellulose through a homogeniser was increased from 3 to 5 passes.^{[91](#)} This contradicts the conclusions of Padberg and co-authors where it was suggested that decreasing oxygen transmission rate was partially due to fewer aggregates of fibres.^{[58](#)} This may be due to the carboxymethylation pre-treatments leading to smaller fibril diameters than the initial coarsest samples used in other studies on mechanical only treatments.^{[23,58,80,88](#)} Therefore, increasing degree of fibrillation by increasing the number of mechanical treatment stages on the carboxymethylated cellulose did not lead to an improved oxygen barrier, possibly because the surface area of the cellulose and degree of degradation was already high enough to assemble a network with no connecting porosity and therefore continuing to decrease fibril diameter did not affect barrier properties.^{[26](#)} This agrees

Table 2.5

Length, degree of polymerisation (DP) and Crystallinity index (CrI) of MFC samples used in oxygen barrier testing in⁹³.

Length/ nm	DP	CrI
200	250	0.56
680	350	0.59
1100	400	0.64

with the conclusions of Naderi and Lindström⁸⁵ that when the degree of fibrillation reaches a high enough level, further treatment of the cellulose does not improve barrier properties.

A similar study can be seen from Naderi and co-authors where carboxymethyl cellulose was grafted to cellulose fibres as a pre-treatment before passing through a microfluidiser with increasing number of passes. After 1 pass the oxygen transmission rate was too high to be measured but after 5 passes was very low, suggesting that after 1 pass through the microfluidiser, the MFC was not fibrillated enough to form a dense network.⁹² The results may be different from Aulin and co-authors²⁶ and Siró and co-authors⁹¹ because possibly the carboxymethyl cellulose grafting pre-treatment was not as effective at dispersing fibrils as the carboxymethylation of cellulose, resulting in an initial sample with a low degree of fibrillation compared to the other studies.

Similarly Naderi and co-authors phosphorylated cellulose and then microfluidised with increasing number of passes.⁹⁴ The study found that the MFC sample made from cellulose with the lowest degree of phosphate substitution did not form a measurable oxygen barrier after 1 pass through the microfluidiser but did form an effective oxygen barrier after 2 passes. This suggests that the increased degree of fibrillation from the additional microfluidization pass produced a network of MFC with little connecting porosity. However, increasing to 6 passes through the microfluidiser led to a failed reading for oxygen permeability at 80% RH and an increase in OP at 50% RH. The authors suggested this could be due to a reduction in fibril length from over processing, which was supported by AFM images of the MFC samples.⁹⁴

An interesting study which purposefully examined whether increasing mechanical processing can degrade barrier properties of films was performed by Fukuzumi and co-authors.⁹³ A TEMPO mediated oxidation pre-treatment was applied to cellulose fibres, followed by the application of three different mechanical treatment methods. The aim was to vary intensity of the mechanical treatment to intentionally cut the fibrils so that the effect of fibril length on barrier properties could be studied. The study found no difference in water vapour permeability of thin layers of MFC coated on PET, but did find that the longer fibrils had a lower oxygen permeability which the authors suggested was due to higher crystallinity. This study suggests that decreasing the length of the fibrils has some impact on the gas barrier properties. Therefore, it may be that decreasing fibril width is not the only factor that affects barrier properties- potentially a high fibril length and crystallinity is also needed. Table 2.5 shows the measured average fibril lengths, the degree of polymerisation and crystallinity index. The results show that the oxygen transmission rate began to increase as the length decreased below 1100 nm, the degree of polymerisation below 400 and the crystallinity index below 0.64.⁹³

The effect of fibril length was not extensively discussed in other studies, which may be due to difficulties in measuring fibril length.⁸⁵ Kumar and co-authors found that a TEMPO oxidized MFC sample formed films with improved barrier properties after a second homogenization stage compared to the first despite no visible decrease in fibril diameter and a decrease in length. However, the authors suggested that the alkaline TEMPO oxidation treatment used in this case was harsh which resulted in rigid, rod like particles. Potentially, the homogenization

stage increased their flexibility.⁸⁸ An observation from Naderi and co-authors⁹⁴ that increasing number of passes through a microfluidiser after phosphorylation of cellulose increases the OP of MFC films, possibly due to a reduction in fibril length, supports the findings of Fukuzumi and co-authors.⁹³

2.4.2 The Effect of Chemical or Enzyme Pre-treatment

The Influence of TEMPO Mediated Oxidation on the Barrier Properties of MFC

The results from studies discussed in the next section investigate the effect of TEMPO mediated oxidation on the barrier properties of MFC films or coatings compared to mechanical treatments only. Literature findings are summarized in Table 2.6.

Table 2.6

Findings from literature studies discussing the effect of TEMPO mediated oxidation on gas barrier properties compared to mechanical only treatments.

Reference	MFC production	Findings
⁸⁸	MFC produced through TEMPO mediated oxidation and homogenizing compared to MFC produced through refining or refining followed by grinding in a Supermasscolloider.	OTR similar for different samples and WVTR lower for samples produced only mechanically.
⁹⁵	Refining followed by microfluidization or TEMPO oxidation followed by microfluidization.	TEMPO mediated oxidation did not result in lower WVTR compared to mechanical treatment only.
⁸⁶	TEMPO mediated oxidation followed by homogenizing	TEMPO mediated oxidation decreased OTR compared to mechanical treatments only.
⁸¹	TEMPO mediated oxidation followed by grinding compared to grinding with Supermasscolloider only	TEMPO mediated oxidation sample had similar OTR to mechanical only samples.
⁶⁹	TEMPO mediated oxidation MFC compared to a commercial mechanical only MFC	TEMPO mediated MFC sample had significantly lower OP.
⁹⁶	MFC made through TEMPO mediated oxidation compared to MFC made through mechanical treatment only	Coatings of each sample had a similar OP.

Jimenez-Lopez and co-authors⁹⁵ and Kumar and co-authors⁸⁸ showed that films made from mechanically produced MFC can form a superior water vapour barrier to TEMPO oxidised samples. In addition, Bessonoff and co-authors⁸¹, Guivier and co-authors⁹⁶ and Kumar and

co-authors⁸⁸ found that there was no significant improvement in oxygen barrier properties for films made from TEMPO mediated oxidation MFC compared to mechanical only MFC when accounting for variation in measurements. This could be for several reasons. Jimenez-Lopez and co-authors suggested that the difference could be due to a reduced crystallinity of the cellulose measured in their study following the TEMPO mediated oxidation process. The authors also proposed that the additional carboxyl groups created by the TEMPO mediated oxidation process lead to a stronger interaction with water vapour and this is what increases the WVP. This hypothesis was supported by fitting of water vapour sorption isotherms which showed that there was a stronger tendency to bind water for TEMPO mediated oxidation samples.⁹⁵ Kumar and co-authors suggested that the TEMPO mediated oxidation process may reduce the flexibility of the cellulose, therefore reducing entanglements within the network.⁸⁸ This is similar to the argument used by Belbekhouche and co-authors when MFC films were found to have superior oxygen barrier properties to CNC films due to a more entangled network forming.⁷³

In contrast, the influence of TEMPO oxidation was also shown by Fukuzumi and co-authors where films or thin coatings of TEMPO oxidised MFC formed significantly better oxygen barriers than an MFC material with more coarse particles present.⁶⁹ This result was also seen by Chinga-Carrasco and Syverud where a TEMPO mediated oxidation pre-treatment decreased OTR of films compared with mechanical only MFC.⁸⁶ Possibly the difference in findings between these studies and those discussed previously was linked to the extent of delamination of the mechanical only treated samples. If large fibre fragments were present in the mechanical only treated samples used in these studies, this could cause defects in the film and reduce the ability for the MFC to form a gas barrier, as seen by Herrera and co-authors.⁸⁴

The Effect of Carboxymethylation or Enzyme Pre-treatment on Barrier Properties of MFC

Studies discussing the use of a carboxymethylation or enzyme pre-treatment prior to a mechanical fibrillation stage as a way to improve barrier properties are summarized in Table 2.7.

The effect of carboxymethylation pre-treatment on the barrier properties of MFC coated paper or cardboard was evaluated by Yook and co-authors³¹ and Zhang and co-authors⁹⁷. Yook and co-authors found that an MFC sample made through carboxymethylation followed by grinding in a Supermasscolloider produced coatings with lower OTR and similar WVTR to MFC made through mechanical only treatments. The authors suggested this was due to the smaller diameter of the carboxymethylated samples viewed in SEM images of the MFC coated paper leading to a more dense network that could prevent the transport of oxygen. However, the carboxymethylated MFC coatings had similar WVTR values to the mechanical only MFC coatings which was suggested to be due to hydrophilicity of the cellulose layer meaning that increasing density did not reduce WVTR.³¹ Similarly, Zhang and co-authors found that an MFC sample made with a carboxymethylation pre-treatment had a higher WVTR than an MFC produced through mechanical treatment only. Air permeability of the carboxymethylated sample was lower, suggesting the carboxymethylated MFC formed a denser coating layer.⁹⁷ This suggests the carboxymethylation reaction could have increased the interaction between cellulose and water and therefore, despite a more fibrillated MFC sample, the barrier properties to water vapour did not improve.

Chinga-Carrasco and co-authors studied how carboxymethylation of cellulose fibres prior to homogenization affected the oxygen barrier properties of MFC films. A lower oxygen transmission rate was measured for carboxymethylated MFC. This was thought to be due to

Table 2.7

Findings from literature studies discussing the effect of carboxymethylation or enzyme treatments on gas barrier properties compared to mechanical only treatments.

Reference	MFC production	Findings
³¹	MFC produced through Supermasscolloider only or MFC produced by carboxymethylation followed by Supermasscolloider.	WVTR similar for both coatings but MFC coatings with carboxymethylation pre-treatment had lower OTR.
⁷⁸	Carboxymethylation followed by homogenization.	MFC films with carboxymethylation treatment had lower OP.
⁹⁷	Grinding with Supermasscolloider with or without carboxymethylation pre-treatment.	Carboxymethylated MFC coated papers had higher WVTR than MFC coatings produced through mechanical treatment only.
⁹⁸	Refining and homogenization with or without an endoglucanase enzyme pre-treatment.	Enzyme pre-treatment reduced OTR of MFC films.

the higher proportion of nano sized fibres and fewer large fibre aggregates observed in SEM images of the MFC films.⁷⁸ This agrees with the results from Yook and co-authors³¹ and implies that the reduction in fibril size resulting from the carboxymethylation pre-treatment can result in a network of fibrils with increased tortuosity of the pore connectivity and therefore slow the transport of oxygen gas.

The research of Chinga-Carrasco⁷⁸ and Yook and co-authors³¹ suggest that an increased degree of fibril separation through a carboxymethylation pre-treatment can be useful to improve oxygen barrier if the MFC produced through mechanical treatment only is not fine enough to form a film with no connecting porosity. Padberg and co-authors⁵⁸ suggested that this chemical pre-treatment is not necessary to form an MFC film with optimum oxygen barrier properties. However, a study directly comparing untreated and carboxymethylated pulp fibrillated using identical increasing fibrillation stages would be needed to properly address this question.

Using enzymes instead of carboxymethylation to produce finer MFC, Djafari Petroudy and co-authors studied the effect of an endoglucanase enzyme pre-treatment on the degree of fibrillation and oxygen barrier properties of MFC films made from bleached bagasse pulp. MFC was made through refining followed by homogenization. Films made from the enzyme pre-treated MFC had a lower oxygen permeability than those made through mechanical treatments only. The authors suggested this may be due to the smaller fibril diameter and narrower size distribution of the enzyme pre-treated samples.⁹⁸ Therefore, adding an enzyme pre-treatment to improve fibrillation of MFC and therefore improve oxygen barrier properties may offer a more environmentally friendly alternative to carboxymethylation.

2.4.3 Increasing the Intensity of a Chemical Pre-treatment

Several articles summarised in Table 2.8 have investigated the effect of increasing the intensity of a chemical pre-treatment prior to a mechanical fibrillation or disintegration stage.

Table 2.8

Findings from literature studies increasing the intensity of a chemical pre-treatment

Reference	MFC production	Findings
99	Swelling cellulose fibres using deep eutectic solvent at different temperatures before microfluidizing.	Increasing temperature or treatment time decreases OP of MFC films.
100	TEMPO oxidation with increasing amounts of NaClO added before homogenization	OP decreases as carboxylate content of cellulose increases.
101	TEMPO oxidation with increasing carboxylation through either increasing reaction time or increasing NaClO concentration.	Increased cellulose carboxyl content decreased OTR of thin MFC films.
102	Increasing the quaternary amine content of cellulose prior to homogenizing	Increased quaternary ammonium content increased OP.
103	TEMPO mediated oxidation or TEMPO mediated oxidation followed by mixing $Et_4N(OH)$. After homogenizing, $Et_4N(OH)$ modified cellulose was mixed into TEMPO oxidised cellulose suspensions at increasing ratios.	Increasing NEt_4^+ content of cellulose increased WVP and OP.
94	Phosphorylation followed by microfluidizing	Effect of increasing phosphorylation depended on RH and on number of passes through microfluidiser.
104	TEMPO mediated oxidation followed by periodate oxidation. Sheets made and fibrillated by increasing pH to 12.	Immersion in pH 12 solution before drying led to decreased OP.
105	Increasing degree of periodate oxidation followed by refining and microfluidizing.	Increasing periodate oxidation increased OP and WVP at 50% RH but OP and WVP of periodate modified samples were lower at 80% RH.

A study by Wu and co-authors used a TEMPO mediated oxidation pre-treatment to produce MFC where the degree of fibrillation was altered by increasing the concentration of NaClO before homogenization which increased the cellulose carboxylate content from 0.5 to 1.8 mmol g⁻¹. This increase in carboxyl content increased fibril surface charge, therefore increasing electrostatic repulsion and helping fibrils to separate. Oxygen transmission rate was lower for thin films of high carboxylate content MFC on a PLA substrate.¹⁰⁰ Similarly, Rodionova and co-authors increased the cellulose carboxyl content from 0.4 to 1.4 mmol g⁻¹ during TEMPO mediated oxidation through either increasing NaClO concentration or increasing the reaction time. The authors also found a reduction in oxygen transmission rate of thin films of MFC coated onto PET as the reaction time or concentration of NaClO increased.¹⁰¹ Both studies linked the decrease in oxygen transmission to smaller fibril diameters or decreased number of fibre fragments as a result of increased electrostatic repulsion between fibrils during the mechanical disintegration phase caused by the increased number of carboxylate groups. Saito and co-authors found that a carboxyl content of 1.5 mmol g⁻¹ corresponded to the oxidation of the C6 hydroxyl group to a carboxyl group on every second glucose unit on the external surface of the 3-4 nm diameter microfibrils.⁵⁵ Possibly the increased NaClO concentration used by Wu and co-authors¹⁰⁰ (2-10 mmol g⁻¹ of cellulose) compared to Saito and co-authors⁵⁵ (1.3-5 mmol/ gram of cellulose) could have led to oxidation of hydroxyl groups within the fibrils.

A different approach to increasing the degree of fibrillation was used by Sirviö and co-workers who used a deep eutectic solvent made of choline chloride and imidazole to treat cellulose fibres at increasing temperatures before microfluidization to increase swelling of the cellulose fibres and allow easier fibrillation into MFC. The research showed that fibres treated at increasing temperatures had smaller fibril diameters due to higher swelling in the pre-treatment phase and films made from these materials had lower oxygen permeability.⁹⁹ This is further evidence that increasing the intensity of chemical treatments meant to help separate fibrils results in a decreased fibril width which then leads to lower oxygen permeability of films.

In contrast to the above results, Larsson and co-authors increased the degree of periodate oxidation of cellulose by increasing reaction time prior to fibrillating by refining followed by microfluidizing. This led to an increase in oxygen and water vapour permeability at 50% RH as the dialdehyde cellulose content increased. The authors linked this to a significant decrease in the degree of cellulose crystallinity resulting from the periodate oxidation process. Furthermore, a fibrillar structure was not visible in SEM images of films made from MFC with the highest dialdehyde cellulose content, suggesting that severe degradation of the cellulose had taken place. However, at 80% RH, the WVP and OP of periodate oxidised MFC was lower than that of untreated MFC. The authors suggested that the cross linking between dialdehyde cellulose units was important in preventing swelling at high humidity and therefore maintaining barrier properties.¹⁰⁵ This research shows that maintaining crystallinity and cellulose structure can be beneficial to barrier properties but these effects can be less significant at high RH than the benefits of decreasing moisture sensitivity of cellulose.

An innovative method to produce an MFC film was used by Gorur and co-authors through performing TEMPO mediated oxidation on cellulose followed by periodate oxidation, forming a sheet through vacuum filtration and then increasing the pH to introduce charges, break hemiacetal links and fibrillate the fibres. A reaction scheme is shown in Figure 2.3. A substantial decrease in oxygen permeability was seen for the sheets immersed in pH 12 solution before drying compared to sheets made without this stage. This was due to the extensive fibrillation of the cellulose compared to the pre-treated pulp fibres in their uncharged form. The increased fibrillation was clearly visible in SEM images of the film surfaces. Despite increased charge on the cellulose and breakage of the hemiacetal cross linkages caused by increasing the pH,

the OP was still lower for the fibrillated samples at 80% humidity.¹⁰⁴ This result was different from that of Larsson and co-authors, who found that cross linkages from periodate oxidation likely prevented swelling at high humidity and helped to maintain barrier properties.¹⁰⁵ This could be because the degree of fibrillation of the samples was very different in the case of Gorur and co-authors¹⁰⁴ so the difference in density of the film had more of an effect on the transmission of oxygen than the increase in swelling from breaking the cross linkages.

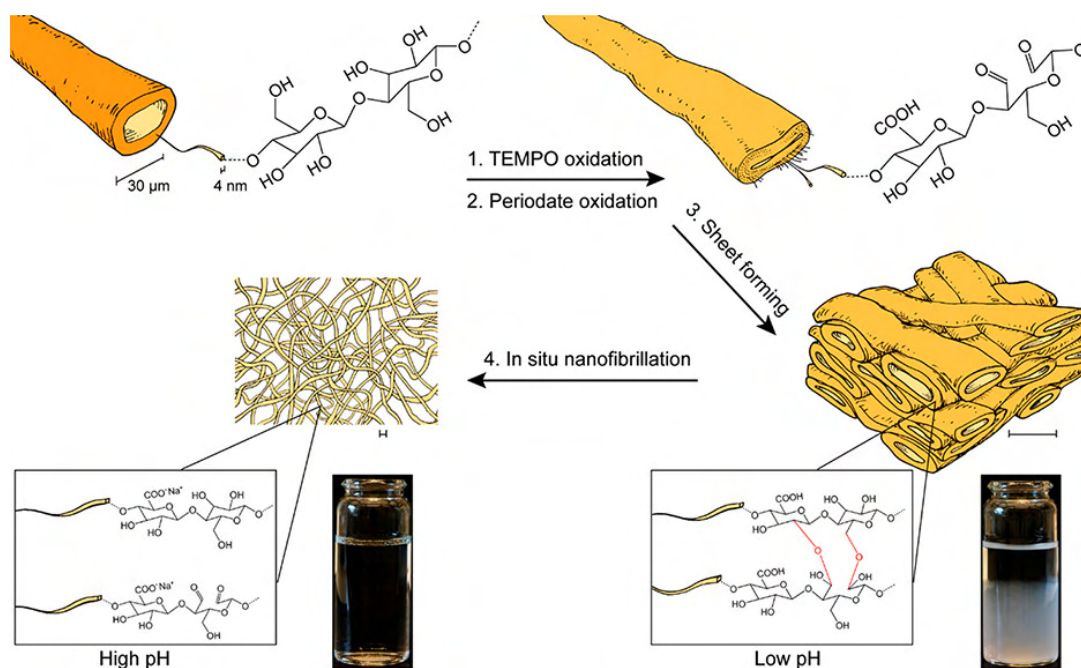


Fig. 2.3. Reaction scheme for TEMPO mediated oxidation of cellulose followed by periodate oxidation followed by increasing pH to 12 (unmodified from original). From Gorur YC, Larsson PA, Wågberg L (2020) Correction to "self-fibrillating cellulose fibers: Rapid in situ nanofibrillation to prepare strong, transparent, and gas barrier nanopapers". *Biomacromolecules* 21(8):3479–3479, <https://doi.org/10.1021/acs.biomac.0c00997>, Copyright © 2020 American Chemical Society, with CC-BY, license information and disclaimer or warranties available at: <https://creativecommons.org/licenses/by/4.0/legalcode>

Table 2.9

Effect of the fibrillation process described by¹⁰⁴ on measurements of oxygen permeability of MFC films.

	Oxygen permeability at 50% RH ($\text{cm}^3 \mu\text{m m}^{-2} \text{d}^{-1} \text{kPa}^{-1}$) % RH	Oxygen permeability at 80% RH ($\text{cm}^3 \mu\text{m m}^{-2} \text{d}^{-1} \text{kPa}^{-1}$)
Unfibrillated	1.6	8.4
Fibrillated	0.7	2.4

Similar to Rodioniva and co-authors¹⁰¹ and Wu and co-authors¹⁰⁰, Naderi, Lindström and co-authors (2016)⁹⁴ increased the intensity of a chemical pre-treatment but achieved this using a phosphorylation reaction rather than carboxylation to add negatively charged groups to cellulose fibres in order to increase separation into fibrils via increased electrostatic repulsion. Naderi, Lindström and co-authors (2016) found that when the degree of substitution of

the phosphate group on cellulose increased, the resulting effect on the oxygen permeability of MFC films made from the phosphorylated cellulose was complex. For example, samples made with only one pass through the microfluidiser showed an initial decrease in OP as degree of substitution increased followed by an increase in OP after a further increase in degree of substitution. For samples made from 2 passes through the microfluidiser, increasing phosphorylation decreased OP- particularly for the measurements at 80% RH. There was an increased nanofraction measured through centrifugation as the degree of substitution increased due to the negative charges on the phosphate groups aiding fibrillation. Potentially after only one pass through the microfluidiser, the fibrillation was relatively low and the network was not strong enough to prevent swelling in the increased RH during oxygen barrier testing. Increasing the cellulose charge by increasing the degree of substitution may not have had a negative impact on oxygen barrier for more fibrillated samples because maybe the high degree of fibrillation had a higher impact.⁹⁴

Conversely, there has also been research into increasing the intensity of positive charge on functionalised cellulose with the aim to improve barrier properties of MFC films. Ru and co-authors produced MFC from bamboo pulp by adding a quaternary amine group with increasing degree of substitution to cellulose and therefore increasing positive charge prior to homogenizing. Increasing positive charge initially decreased the oxygen transmission rate of thin layers of MFC coated onto PLA, but further increasing the charge increased the oxygen transmission rate despite the higher charged MFC having a smaller fibril diameter.¹⁰² The authors suggested that this could be linked to the decrease in density of films as the cellulose charge content increased since the quaternary amine groups are not able to take part in the hydrogen bonding between fibrils and the methyl groups around the nitrogen provide significant steric hindrance which could prevent other hydrogen bonding interactions between available hydroxyl groups and reduce close packing of the cellulose. This decrease in bonding through the large bulky amine group prevented increasing the degree of fibrillation of cellulose from improving barrier properties.¹⁰²

Similarly, Kubo and co-authors¹⁰³ mixed TEMPO oxidised MFC with increasing amounts of MFC produced by adding $Et_4N(OH)$ after TEMPO mediated oxidation prior to homogenizing. Film density decreased as the molar ratio of Et_4N^+ increased. This corresponded with an increase in both oxygen and water vapour permeability. The authors suggested that the bulky alkyl groups introduced steric hindrance and may have weaker intermolecular forces than the hydrogen bonds present between carboxyl groups in TEMPO oxidised cellulose.¹⁰³ The studies of Ru and co-workers¹⁰² and Kubo and co-workers¹⁰³ showed that there can be unintentional changes to the structure of MFC networks as a result of functionalising the cellulose to introduce electrostatic charges. If the functional group added to the cellulose provides sufficient steric hindrance, it may interfere with bonding between and close packing of the cellulose fibrils which could have a larger impact than decreasing fibril diameter. Potentially the conflicting results seen by Naderi and co-authors⁹⁴ could also have been influenced by steric hindrance from the phosphate groups preventing close packing of fibrils and therefore leading to some increases in OP as the degree of phosphate substitution increased.

2.4.4 Comparisons of Different Pre-treatments

Comparison of Carboxymethylation with Other Pre-treatments

Research into the effects of carboxymethylation compared to other pre-treatments aiming to increase the degree of fibrillation of cellulose is summarised in Table 2.10.

Table 2.10

Findings from literature studies comparing enzyme and carboxymethylation pre-treatments

Reference	MFC production method	Findings.
68	Compared carboxymethylation with enzyme treatment and refining as pre-treatments to homogenizing.	WVP higher but OP lower for enzyme treated sample
106	Carboxymethylation compared with enzyme treatment and refining as pre-treatments to homogenizing	No significant difference in OP between samples when considering variation.
35	Compared enzyme treatment and refining, carboxymethylation and the grafting of carboxymethyl cellulose all before microfluidization.	CMC modified sample had higher OP than enzyme treated and carboxymethylated.
107	Carboxymethylation or enzyme pre-treatment followed by microfluidizing	Carboxymethylated MFC films had lowest OP.
108	Compared alkoxylation with a carboxymethyl group with a carboxyethyl group before microfluidizing.	MFC modified with carboxyethyl group had higher OP.
109	Carboxymethylation or sulfoethylation followed by microfluidization	Carboxymethylated sample had lower OP.
94	Carboxymethylation or phosphorylation prior to microfluidizing	Both pre-treatment stages produced MFC films with similar OP values.

The studies of Minelli and co-authors⁶⁸ and Plackett and co-authors¹⁰⁶ compared oxygen permeability of MFC films made from a carboxymethylation or enzyme treatment each followed by homogenization. Plackett and co-authors found no significant difference in oxygen permeability between the two types of MFC films. The authors suggested that although the fibril diameter of the carboxylated MFC was lower, it contained large fibre fragments which may have disrupted the MFC network.¹⁰⁶ However, Minelli and co-authors found that the films made from enzyme treated MFC had lower oxygen permeability and a higher density. In spite of the lower oxygen permeability, the authors measured lower oxygen diffusivity in the carboxymethylated MFC films. The measurement of oxygen diffusivity is not common so it is difficult to compare this to other studies. Minelli and co-authors also found that the water vapour permeability and diffusivity was lower for the carboxymethylated samples, which was thought to be because this MFC had smaller fibril diameter and a narrower size distribution which led to higher tortuosity in the gas diffusion path.⁶⁸

A study by Fall and co-authors also compared an enzyme pre-treatment with a carboxymethylation pre-treatment prior to microfluidization. The authors found that the carboxymethylated MFC had the finest structure from AFM imaging along with the highest light transmittance solution and highest viscosity, all indications that this sample had the highest degree of fibrillation. As expected from the higher degree of fibrillation, the carboxymethylated MFC films had the lowest oxygen permeability.¹⁰⁷ This contrasts with the results from Plackett and co-authors¹⁰⁶ which found no significant differences in OP between MFC films produced from carboxymethylated and enzyme treated MFC. An investigation by Naderi, Lindström and co-authors (2017)³⁵ also compared enzyme treated with carboxymethylated MFC with the additional comparison point of MFC produced with a CMC grafting pre-treatment. In all cases, microfluidization was used as the mechanical disintegration step. The carboxymethylated MFC had a higher percentage of nano sized fraction measured by the solids content of the supernatant after centrifuging, but the enzyme pre-treated MFC had the lowest oxygen permeability, agreeing with the results seen by Minelli and co-authors.⁶⁸

Naderi, Lindström and co-authors (2017)³⁵ suggested that the differences in oxygen permeability between films made from MFC produced through different methods could be due to the higher surface charge on the carboxymethylated MFC sample leading to stronger interaction with water vapour during the oxygen transmission rate test.³⁵ Since the test was performed at 50% relative humidity, there would have been some moisture present in the testing chamber which could adsorb to the cellulose. In fact, Meriçer and co-authors measured moisture vapour adsorption isotherms of the MFC films and found that the films produced from carboxymethylated MFC sorbed more moisture vapour due to the higher surface charge. The additional sorbed moisture vapour can increase swelling of the film.¹¹⁰ A higher water sorption for the carboxymethylated MFC film was also seen by Minelli and co-authors.⁶⁸ Figure 2.4 shows that there is a significant increase in oxygen permeability between 0 and 0.5 water activity (corresponding to 0% and 50% RH). Variation in the results is too large to conclude that carboxymethylated MFC OP increases differently than enzyme treated MFC with changing RH. However, water sorption data clearly showed that water sorption was higher for carboxymethylated MFC.

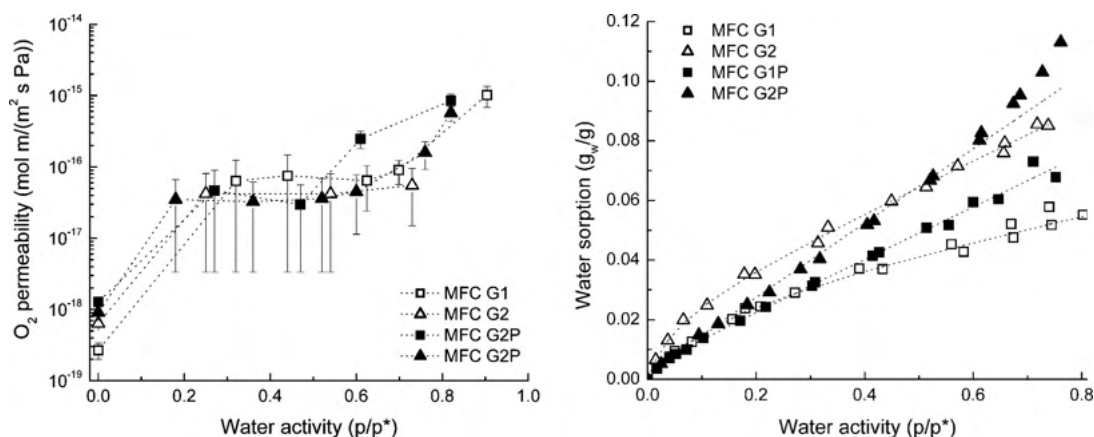


Fig. 2.4. Variation in water sorption and oxygen permeability with increasing water activity for MFC films. MFC G1 refers to MFC made through enzyme treatment and refining followed by homogenizing and MFC G2 refers to MFC made by carboxymethylation followed by homogenizing. G1P and G2P refer to plasticized versions of the same MFC samples. Reprinted from: Journal of Membrane Science, 358 (1-2), M. Minelli, M. Giacinti Baschetti, F. Doghieri, M. Ankerfors, T Lindström, I. Siró, D. Plackett, *Investigation of mass transport properties of microfibrillated cellulose (MFC) films*, 67-75, Copyright (2010), with permission from Elsevier.

The potential detrimental effect of surface charge on oxygen permeability was also seen by Naderi, Larsson and co-authors where the authors used an alkoxylation treatment using firstly the standard monochloro acetic acid (MCA) to produce a carboxymethylation reaction and then used 2-chloro propionic (CPA) acid to increase the size of the charged groups added to the cellulose fibres.^[108] The use of the CPA reagent resulted in a higher fraction of nano sized cellulose fragments and higher viscosity suspensions. However, the oxygen permeability of the MCA treated MFC was lower than the CPA treated MFC. The authors suggested this was due to the oxygen permeability testing taking place under 50% or 80% relative humidity and the fact that the surface charge and water retention values were higher for the CPA treated MFC. Therefore, this may have led to a stronger interaction with water vapour, causing swelling of the film and disruption of the network which allowed higher transmission of oxygen.¹⁰⁸ This agrees with the results seen by Naderi, Lindström and co-authors (2017)³⁵ where a more highly charged MFC sample made films with higher oxygen permeability despite a higher degree of fibrillation. However, the decreased OP for the MFC with the larger size alkoxy group seen by Naderi, Larsson and co-authors¹⁰⁸ could also be due to increased steric hindrance from the bulkier group preventing close packing of the fibrils, as seen by Ru and co-authors.¹⁰² Naderi, Koschella and co-authors¹⁰⁹ and Naderi, Lindström and co-authors (2016)⁹⁴ compared sulfoethylation or phosphorylation to carboxymethylation of cellulose as a pre-treatment to microfluidizing. Naderi Lindström and co-authors (2016) found that carboxymethylated MFC formed films with a similar OP to phosphorylated samples.⁹⁴ However, Naderi, Koschella and co-workers found that the sulfoethylated MFC formed films with higher OP than the carboxymethylated sample despite having a higher percentage of nanofraction fines measured through centrifugation. The viscosity of sulfoethylated MFC suspensions were also higher than carboxymethylated samples, further suggesting a higher degree of fibrillation for the sulfoethylated MFC. However, AFM images showed that fibril length and width for the two samples were similar. The authors suggested that the sulfoethylated MFC may have been more prone to swelling and this could be why the OP was higher at 50% and 80% RH. Steric hindrance from the large sulfoethyl groups may also have contributed to a lower OP.¹⁰⁹

2.5 | Discussion

Literature studies looking at how MFC pre-treatments affect gas barrier properties have varying results. There is no straightforward relationship between increasing degree of fibrillation of MFC, through either increased mechanical processing or adding a chemical pre-treatment, and improving gas barrier properties. For samples where only mechanical treatments were used, increasing the intensity of the mechanical treatment can improve gas barrier properties but there is a plateau in this effect. This was seen by Juntunen⁸², Padberg and co-authors⁵⁸, and Wei and co-authors⁸³. Once the MFC network has no connecting porosity, further fibrillating the cellulose may not show any benefit to gas barrier properties⁵⁸. For samples with a chemical or enzyme pre-treatment, increasing mechanical processing may not improve gas barrier properties because the MFC network can already be dense enough that increasing fibrillation does not further reduce gas transport.²⁶ This effect was seen by Aulin and co-authors²⁶ and Siró and co-authors⁹¹. In fact, applying too much mechanical treatment can be detrimental to barrier properties by reducing length and crystallinity of fibrils, an effect seen by Fukuzumi and co-authors.⁹³

Increasing the degree of fibrillation by increasing the intensity of a chemical pre-treatment can be effective in improving barrier properties. For example, Rodionova and co-authors¹⁰¹ and Wu and co-authors¹⁰⁰ found that increasing intensity of TEMPO mediated oxidation reduced oxygen permeability of MFC films. However, if the chemical pre-treatment involves adding bulky groups, this may be detrimental to close packing of fibrils due to steric hindrance, as seen by Ru and co-authors¹⁰². Furthermore, chemical pre-treatments often introduce negative charges to help fibrillate the cellulose and these negative charges can lead to stronger interactions with water vapour, therefore increasing WVP or decreasing OP at high RH. This effect was suspected by Naderi, Lindström and co-authors (2017)³⁵ when an enzyme treated sample with a supposedly lower degree of fibrillation than a carboxymethylated formed better oxygen barriers at 50% RH. For this reason, chemical pre-treatments that act to reduce swelling such as periodate oxidation were found by Larsson and co-authors to be most effective at reducing oxygen permeability at high relative humidity. However, using a periodate oxidation reaction with a high rate of conversion can lead to a decrease in barrier performance, potentially due to a decrease in cellulose crystallinity.¹⁰⁵

Cellulose crystallinity may have some influence on the barrier properties of MFC films but this appears to be a less important effect than fibrillation. If pre-treatments reduce crystallinity but increase fibrillation, the gas barrier properties may still improve or remain constant. This effect was seen by Padberg and co-authors⁵⁸ and Siró and co-authors⁹¹ and Wei and co-authors⁸³. However, if crystallinity is decreased without a significant increase in fibrillation, Larsson and co-authors¹⁰⁵ showed that this may have a negative effect on barrier properties. It is difficult to precisely understand how the crystallinity of MFC affects the gas barrier properties of films and coatings because processes that alter the crystallinity of the cellulose also often change the morphology of the material. Furthermore, it is difficult to quantitatively compare crystallinity index of cellulose materials.⁵⁷

The source of the cellulose used to make the MFC may also have some influence on how degree of fibrillation relates to barrier properties. For example, Kumar and co-authors found that there were differences in OTR between MFC films made from hardwood and softwood pulp.⁸⁸ In addition, Yook and co-authors found that unbleached kraft pulp formed a less effective barrier to oxygen than bleached kraft pulp under the same fibrillation conditions, suggested to be because the unbleached MFC had larger fibril diameters.³¹ Rodionova and co-authors treated both spruce and eucalyptus pulp with TEMPO mediated oxidation followed by homogenisation and found that the spruce based MFC formed films with lower OTR than the eucalyptus based

MFC after the same chemical and mechanical treatments on the cellulose.¹⁰¹ Therefore, pulp type or cellulose source may influence the effect of fibrillation on barrier because different pulp types may reach a different degree of fibrillation under fixed chemical or mechanical conditions. For example, Maliha and co-authors found that the WVTR of films made from bleached eucalyptus kraft pulp was lower than that of bleached pine pulp when the material had been processed in the same way, possibly due to less efficient fibrillation of the longer, thicker pine fibres.¹¹¹ The cellulose source may also affect the crystallinity and degree of polymerisation of the cellulose which may influence the barrier properties. Therefore, another factor complicating the relationship between degree of fibrillation and gas barrier properties may be the use of different pulp types.

In many cases in this review, it has been difficult to conclusively state whether increasing fibrillation has an effect on barrier properties because variation in the oxygen barrier results can be greater than the difference in OTR or OP between samples. This may imply that in these cases the increased fibrillation does not have a significant effect on barrier properties. However, other factors can influence this variation. For example, defects in films or coatings such as pinholes or cracks can allow gas transmission.¹¹² These defects may have more of an effect on the rate of oxygen diffusion through the cellulose network than changes in cellulose characteristics and can contribute to high standard deviations in the results. Articles discussed in this review also use different film or coating production methods, which could influence the relationship between fibrillation and barrier properties, for example by affecting the mass uniformity within the layer or the number of defects.

2.6 | Conclusion

The literature review has shown that the relationship between increasing the fibrillation of cellulose and improving the barrier properties of MFC films is not well understood. Furthermore, many of the papers discussed have measured barrier properties of MFC films rather than MFC coatings on a porous base sheet. This thesis aims to address this gap in technical understanding in order to provide recommendations on the level of fibrillation required to produce an MFC sample that will form coatings with excellent barrier properties.

Experimental

3.1 | Microfibrillated Cellulose

This thesis used MFC produced by Fiberlean Technologies Ltd. at their production plant in Cornwall. This MFC is produced through mechanical treatments using a bleached or unbleached kraft pulp suspension in a wet stirred media mill without any chemical pre-treatment. During the milling process, grinding media beads collide and cellulose fibres are cut or fibrillated when they are caught between them.¹¹³ Some MFC samples used in this work were produced in laboratory scale grinders when small amounts of material with specific properties were required. Many MFC samples were produced in a pilot scale batch process and several in full scale continuous processes.

An MFC sample from the University of Maine was also used as a reference sample in some of this work which is produced through multiple stages of refining of bleached kraft pulp.¹¹⁴

3.2 | Pulp Refining

Pulp was refined in a laboratory Valley Beater. 400g of dry pulp bale was soaked for a minimum of 15 hours in filtered tap water- water passed through a 5 μm and a 0.5 μm filter. After this, the soaked pulp mixture was transferred to the Valley Beater, a laboratory refiner, and an additional 12 L of filtered tap water was added. The pulp mixture was mixed for 15 minutes and, following this, a weight was added to the machine to decrease distance between the stationary and rotating plates so that refining of the fibres could occur in the gap.

To monitor the refining level of the pulp, a sample of 450 mL of pulp was taken from the Valley Beater, diluted to 0.3% consistency, and the Canadian Standard Freeness (CSF) was measured. A litre of 0.3 wt% pulp fibre suspension was poured into a testing chamber with a grid on the base. A switch was opened to allow water to drain through the grid where it enters a cone. The cone has a small hole at the bottom and a larger outlet on the edge. If water from a pulp suspension drains through the grid quickly, a larger volume of water will leave the cone through the larger outlet. The volume of water leaving the larger outlet was recorded by catching the flow into a measuring cylinder.¹¹⁵ Corrections were made for variations in temperature from 20°C or variations in pulp consistency from tables devised by Sundrani and co-authors.¹¹⁶

3.3 | MFC Coating

3.3.1 MFC Coating Background

MFC can be challenging to coat onto paper or cardboard. The high viscosity of aqueous MFC suspensions require that the MFC solids content must be low and this introduces a significant

amount of water into the base paper.¹¹⁷ The high viscosity of MFC suspensions and their tendency to rapidly lose water into the base sheet can also make it challenging to achieve a uniform coating onto a dry base sheet.^{118,119}

3.3.2 Manual Laboratory Rod Coating of MFC

The first part of this thesis looked into coating MFC using manual laboratory wire rod coating. This technique uses a steel rod surrounded by wound steel wire to pull a coating formulation down the length of a sheet of paper or cardboard. The coating rods allows control of the coating wet film thickness as different diameters of the wound steel wire directly relate to wet film thickness of the coating. This technique is a simple laboratory scale test which can be used to determine how well a coating will be applied industrially using paper coating methods.¹²⁰ In this work, manual laboratory rod coating of MFC was attempted using wire rods known as K-bars provided by RK Printcoat Instruments. The base paper to be coated was clipped to a board with a soft backing and a line of Scotch tape was placed horizontally across the top of the paper. The set up for the coating process is shown in Figure 3.1. A plastic pipette was then used to deposit a line of the coating suspension across the Scotch tape. The coating suspension could then be pulled down the length of the paper using the K-bar. After coating, sheets were cut with scissors to fit into Rapid Köthen hand sheet driers and dried at 93°C under 1 bar vacuum pressure for 7 minutes or until dry. The section of the sheet to be dried was cut from the centre of the paper to ensure that a uniform area was selected. The base paper used in these coating experiments was the same commercial copy paper used as a coating base in the remainder of the project. Characterisation details are available in Section 3.3.3.

3.3.3 MFC Coating Through Vacuum Filtration

Lab Made Base Sheets

In the initial study looking into how increasing coat weight of MFC affected barrier properties of paper, MFC was deposited onto laboratory made base sheets using vacuum filtration. This process was based on a Fiberlean Technologies laboratory method to simulate industrial coating of MFC onto the wet end of a paper machine.¹²¹ To prepare the pulp for the base sheets, NBSK bleached kraft pulp (80 g) and eucalyptus bleached kraft pulp (320 g) were soaked overnight. The pulp was refined for 13 minutes to achieve a final CSF of 506 mL.

After refining, the pulp suspension was diluted to 0.8 wt% with water and mixed on a Messmer disintegrator for 10 minutes. This was repeated until 40 L of pulp was produced. The pulp was diluted to a consistency of 0.5% for use in sheet making.

A polyacrylamide retention aid (Percol 292S, BASF) was prepared at 0.5 wt% by mixing Percol 292S granules (0.5 g), tap water (97 mL) and Industrial Methylated Spirits (3 g, 95% purity, JML) with a magnetic stirrer for one hour. This was diluted to an 0.08 wt% solution using tap water. The retention aid was added into base sheet pulp immediately before forming at a dose of 0.12 wt% with respect to dry fibre content.

Base sheets were made using a Messmer British laboratory paper sheet former. This is a device is shown in Figure 3.2. The apparatus consists of a metal tube situated over a wire mesh. The metal tube fills with water, and the pulp suspension is poured into the tube. When the tube fills, there is an agitation stage followed by drainage of the suspension onto the wire mesh.

The sheet was then transferred while wet to a separate vacuum filtration device shown in Figure 3.3. The wet sheet was placed onto a wire mesh where a dilute MFC suspension was poured over and drained under vacuum to form an MFC layer coated on the base sheet. The sheets were then dried at 95°C under 1 bar vacuum pressure in a Rapid Köthen hand sheet drier. Precise dilutions and MFC coating amounts can be found in relevant thesis chapters.



Fig. 3.1. Experimental set up for coating paper with MFC using the manual laboratory rod coating method.

Coating onto a Paper Reel Base Substrate

For all sheets following the initial study, the base paper was a reel of commercial copy paper made from bleached kraft pulp and mineral filler with a grammage of 87 g m^{-2} ; thickness measured through digital micrometer of $99 \mu\text{m}$; and filler content, measured through burning in a Carbolite furnace at 450°C for 90 minutes and calculating loss of mass, of 22% wt%.

To coat the base paper with MFC, a circle was drawn around the vacuum filtration mesh and cut out with scissors. This circle was then placed on top of the mesh under a running tap. The vacuum filtration equipment was assembled and the vacuum was switched on for a few seconds to ensure the wet paper was flat against the mesh before the paper was clamped in place with the top part of the equipment. The MFC was then coated as described above by diluting with water (specific volumes provided in relevant chapters), the vacuum was switched on and then the sheet was dried in the Rapid Köthen handsheet driers.

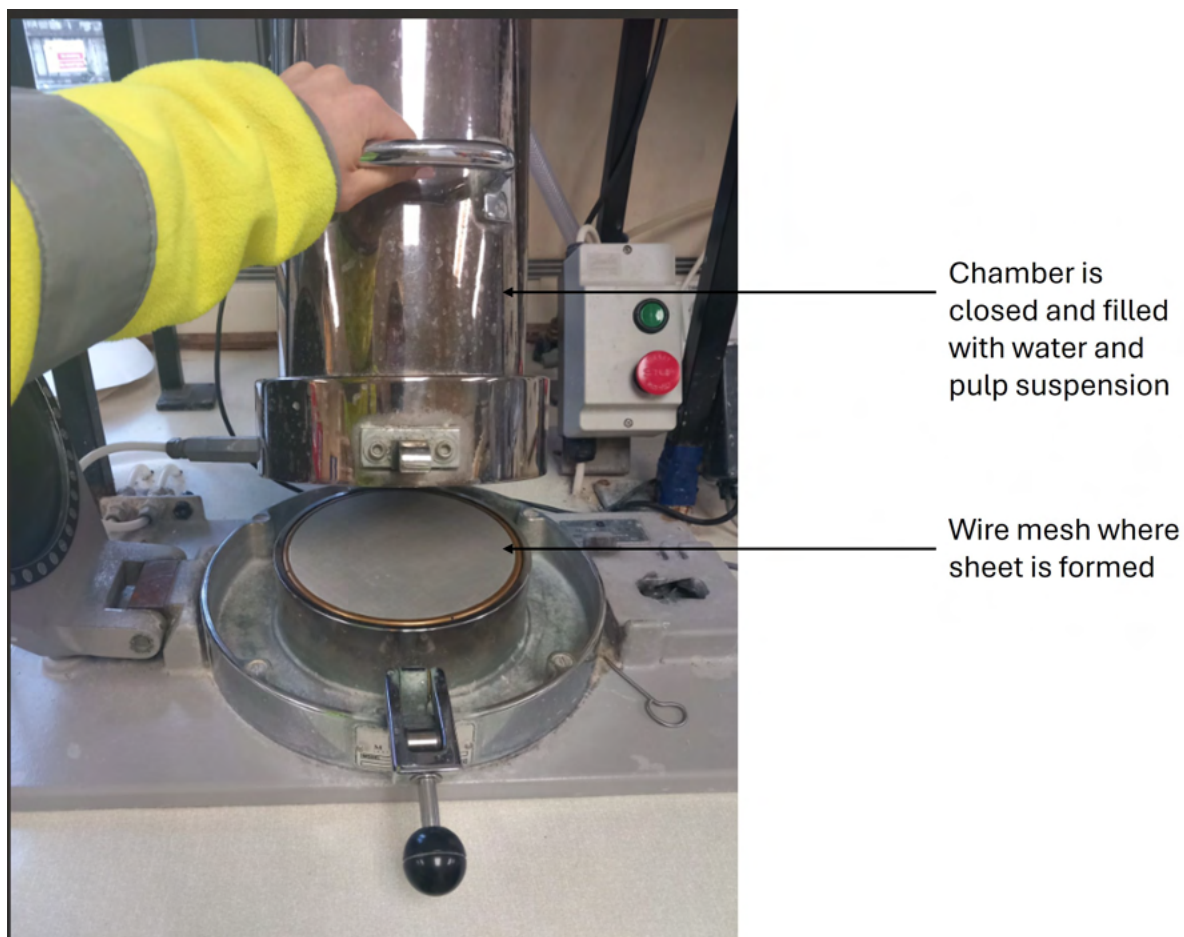


Fig. 3.2. British Messmer handsheet former

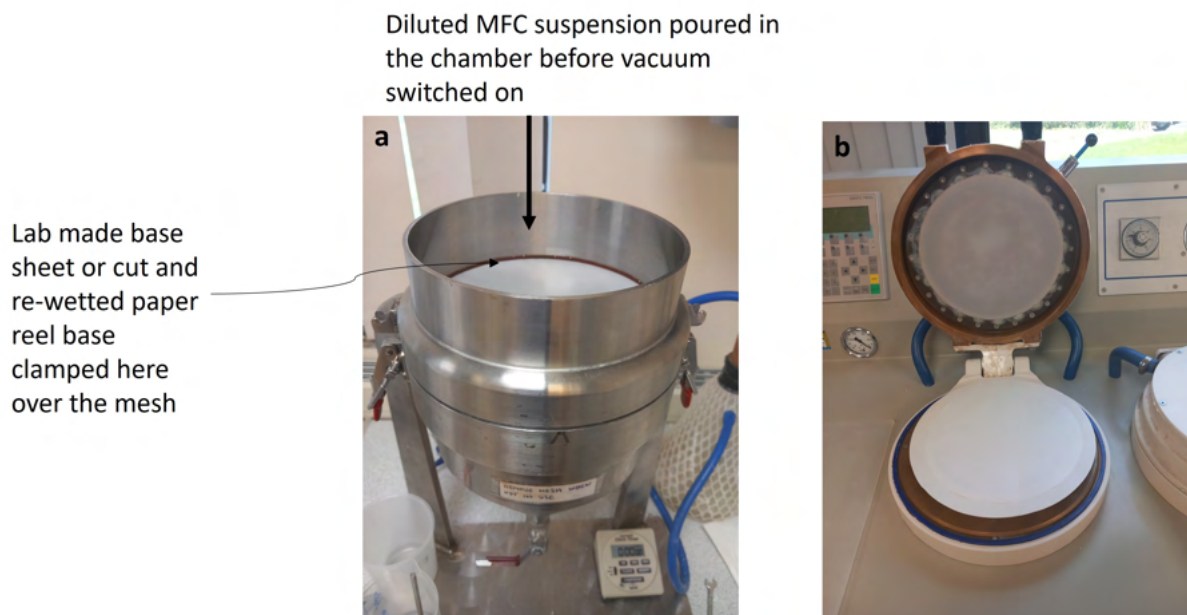


Fig. 3.3. Experimental set up for coating paper with MFC through vacuum filtration. a) Apparatus for vacuum filtration of MFC suspension through base sheet and b) Rapid Köthen hand sheet drier- freshly coated sheet placed between a base and cover sheet before closing lid and drying.

3.4 | Preparing MFC Films

Films of MFC were made using a similar method to coating onto a paper reel base substrate. Instead of a paper reel as a base for vacuum filtration, a SEFAR 11/6 nylon filtration mesh was used to form the MFC films. This mesh is woven with a pore size of 11 μm . The mesh was cut around the mesh of the vacuum filtration device, wetted and laid flat against the mesh of the vacuum filtration device. The MFC was diluted to 0.2% solids and poured into the top chamber of the device. The vacuum was then switched on and the MFC was left to drain until a wet film was formed. At this point, the MFC film was carefully peeled away from the nylon filtration mesh and dried in the Rapid Köthen driers for 7 minutes.

In chapter 7, the film making method was improved by putting the film with the mesh attached into the driers to remove damage caused from peeling the film away from the mesh. The filtrate water was also passed back through the MFC film and allowed to drain to ensure that all the fine particles in the MFC had been incorporated into the film.

Vacuum filtration was chosen as the film formation method because it closely resembles the laboratory method for MFC coating onto paper through vacuum filtration and therefore the structure of the MFC layer is likely to be similar. Film casting, where the MFC suspension was poured into a dish and the water left to evaporate, was attempted multiple times but flat, smooth MFC films could not be reliably produced without the vacuum filtration and Rapid Köthen drying processes.

3.5 | MFC Characterisation methods

3.5.1 Preparing and testing Fiberlean Tensile sheets

The Fiberlean Tensile Fiberlean Tensile (FLT) test was developed by Fiberlean Technologies as a quality control measure for characterisation of MFC. In this test, an MFC suspension is mixed with a ground calcium carbonate (IMERYS IC60) suspension to 20 dry wt% MFC and 80 dry wt% calcium carbonate. A 220 g m^{-2} sheet is made from the suspension through vacuum filtration on a Whatman 40 filter paper. 1 mL of 0.2 wt% polyDADMAC (Sigma-Aldrich) is added to the suspension before filtration to prevent settling of the mineral. Once drained, the sheet is dried in a Rapid Köthen handsheet drier for 7 minutes. The sheets are equilibrated at 23°C and 50% relative humidity for a minimum of 20 minutes. Following this, the sheets are weighed on a 4 decimal place analytical balance and cut with a die cutter into 15 mm wide strips. Tensile strength is then measured using a tensiometer and tensile strength index is calculated from the mass of the sheets and width of the measurement strip using Equation 3.1.¹²² FLT results were provided by Fiberlean Quality Control for the MFC samples described in the current work.

$$\text{Tensile strength index} = \frac{\text{Breaking force}}{\text{Width} * \text{Grammage}} \quad (3.1)$$

3.5.2 Measuring Solids Content of MFC Suspensions

Knowing an accurate solids content of MFC suspensions is essential to accurately apply the correct MFC coat weight to a base sheet, make a film, or measure suspension properties. Solids content of all newly acquired MFC suspensions was measured by oven drying and measuring change in mass. This measurement was performed in triplicate for each MFC sample. Measurements were made on a 4 decimal place analytical balance.

Table 3.1

Fibre and fine parameters provided by a fibre image analyser¹²³.

Measurement	Definition
Lc(n)/ mm	Averaged length of fibres with width greater than 10 μm and less than 75 μm . Includes fibres from 0.05 - 7.6 mm in length.
Lc(l)/ mm	As above but averaged length is weighted by length.
Lc(w)/ mm	As above but averaged length is weighted by weight.
Lc(n, l or w) ISO/ mm	As above for each measurement but including only fibre lengths between 0.2- 7.0 mm
Kink 1/m	Fibre damage per metre for fibres with length greater than 0.2 mm. Kink is defined as a bend in the fibre greater than 15°.
Kink 1/1000	Fibre damage per 1000 fibres
Curl	Fibre curl averaged by length
Fines A/ %	Particles with length below 0.2 mm as a percentage of the total area of particles
Fines B/ %	Length of particles narrower than 10 μm and longer than 0.2 mm as a percentage of the total length of all particles with a length greater than 0.2 mm.
Fibrillation/ %	Area of branching fibrils as a percentage of area of the larger branched particle. Measured only for particles longer than 0.5 mm and wider than 10 μm . A maximum of 20% fibrillation can be measured.
F1- F6 (l)/ %	Percentage of length weighted distribution of fibres. Fibres with width above 10 μm are grouped into fractions based on length: F1: 0-0.2 mm; F2:0.2-0.6 mm; F3: 0.6-1.2 mm; F4: 1.2-2.0 mm; F5: 2.0-3.2 mm; F6: 3.2-7.6 mm
F1- F6 (width, mass, fibrillation)	Fibre fragments described above but parameters are width of fibres in the fraction in μm , mass percentage of fibres in the fraction or fibrillation percentage of fibres in the fraction.

3.5.3 Fibre Analyser Measurements

A Valmet fibre image analyser (Valmet FS5) was used to measure fibre size parameters in dilute aqueous suspension. The instrument operates by capturing greyscale images of fibres and measuring fibre length along the centre of the fibre using optical image analysis. The MFC was diluted to a consistency of 0.002 wt% with tap water prior to analysis. Table 3.1 shows fibre and fine properties given by the fibre image analyser that are relevant to the current research thesis. Fibres between 0.01- 7.60 mm in length can be measured and width can be measured from 0.001- 1 mm.¹²³

3.5.4 Optical Microscopy of MFC Suspensions

MFC suspensions were diluted to 0.08 wt% using tap water. Using a plastic pipette, a drop of diluted MFC suspension was placed on a glass slide. A glass cover slip was carefully laid over the top of the MFC and the slide was left for approximately 15 minutes until some of the water had evaporated, allowing a film of MFC suspension to form between the glass cover slip and glass slide.

For chapters 4, 5, and 6, MFC suspensions were imaged using a Reichert- Jung Polyvar-MET in differential interference contrast mode. A Nikon D5- F1 camera and NIS-Elements software were used to capture images. In chapter 7, a Zeiss Axio imager M2 microscope was used in differential interference contrast mode. Zencore 3.5 software was used to capture images.

3.5.5 Scanning Electron Microscopy (SEM) of MFC

MFC suspensions were diluted using distilled water to 0.001 wt%. Following this, IMERYs microscopy department at Par Moor Centre, Cornwall dewatered 1 mL of the MFC suspensions onto 200 nm pore membranes, sputter coated with platinum and then attached to SEM stubs. SEM imaging was performed at the Bioimaging Centre in the University of Exeter. A Zeiss GeminiSEM 500 microscope along with SmartSEM software was used to obtain images of the MFC. An accelerating voltage of 1.5 kV was used. 20 images each were taken at 500 and 5000x magnification.

3.6 | Rheology of MFC Suspensions

A Malvern Instruments Kinexus Pro+ rotational rheometer combined with rspace software was used to study rheology of MFC suspensions at 25°C. Measurement geometry was a roughened cup and bob with bob diameter 25 mm and length 37.5 mm and cup diameter 27.5 mm and length 62.5 mm (C25 DIN roughened SW120755 and PC DIN roughened C004555).

3.6.1 Investigation into Rheological Characterisation Methods

Rheology could be a useful way to compare different MFC samples since there is often a relationship between rheological properties and degree of fibrillation or aspect ratio of the cellulose. This is because the strength of the network structure in solution is affected by the surface area, flexibility, length and width of the fibrils. However, complexities such as measurement geometry must be considered to reduce the effect of artefacts such as shear banding or wall slip which can occur when there is a layer of low concentration suspension close to the solid surfaces of the measurement geometry.^{60,124–127}

Rotational rheometers can be used with many different measurement geometries such as parallel plates, cone and plate, cup and bob or vane and cup. The use of the parallel plates or cone and plates with MFC suspensions is not considered in this work as is thought to lead to sedimentation of fibrils over time due to gravity.¹²⁶ The effect of wall slip and shear banding is thought to be reduced by using a roughened surface or a cup and vane geometry compared to smooth cup and bob geometry.^{124–126,128} When using a vane geometry, it is assumed that the shear stress is uniform along the cylinder formed by the edges of the blades and the material between the blades moves only with the blades and does not flow. Therefore, the effect of wall slip is reduced because at one surface the suspension is in contact with suspension rather than a solid measurement geometry. The use of a wide cup furthermore reduces the wall slip effect because the stress at the cup edges is low due to the wide gap.^{128–130} However, Nechyporchuk and co-authors found that a concentric cylinder geometry with a serrated surface was necessary to completely prevent measurement artefacts. The authors also found that the edges of the vane blades caused ruptures in the suspension trapped in the gap, causing a non-uniform flow. Additionally, at high shear rates there were irregularities in the vane and cup data compared to other samples which were thought to be caused by movement of suspension trapped within the blades of the vane.¹³⁰

There are several different ways of measuring yield stress of MFC suspensions. Schenker and co-authors measured yield stress through oscillation with an amplitude sweep at 0.5 Hz and determined the yield stress as the associated shear stress where the phase angle increased 5% from the minimum value. It was found that a vane geometry in a large cup showed higher yield stress than a smooth cup and bob or roughened cup and bob which may have been due to some wall slip occurring in the cup and bob measurements. It was also found that for flow curves, samples measured using a vane and cup geometry had higher viscosity which suggests that there were fewer unwanted side effects occurring and the vane measurement system may have been more accurate.⁶⁰ Nazari and co-workers also used oscillation to measure yield stress but with parallel plate geometry. Two values of yield stress were calculated from the oscillation data- the point where the phase angle reaches 45 degrees and the shear stress at the maximum product of shear strain and storage modulus.¹²⁵ Nazari and co-authors also measured yield stress through a shear stress ramp where shear stress is linearly increased over time and the shear stress at maximum viscosity was recorded as the yield stress. This was performed using different geometries, including a vane and cup.¹²⁵ Derakhshandeh co-authors measured yield stress of fibre suspensions using a shear stress ramp where the yield stress was taken at the point of maximum viscosity.¹²⁸

Table 3.2

Gaps between vane and outer cup diameters used by various authors when measuring rheology of MFC suspensions

Reference	Experiment	Gap/ mm
Schenker ¹²⁴	Flow curves and oscillation, rotational rheometer	6.88
Nazari ¹²⁵	Shear stress ramp, rotational rheometer	15.8 ¹³¹
Varanasi ¹²⁷	Haake Rotovisco Rv20, Shear stress ramp	34
Derakhshandeh ¹²⁸	Rotational rheometer, Shear stress ramp, pulp.	61.5
Mohtaschemi ¹²⁹	Brookfield viscometer, flow curve	54.11 or 49.82
Nechyporchuk ¹³⁰	Rotational rheometer, flow curves,	27

In the examples described above, the diameter of the vane was significantly smaller than the cup diameter. Measurement gaps between blade diameter and cup diameter used by various authors are shown in Table 3.2.

In order to compare the rheological properties of MFC suspensions made from different materials, it was important to understand the best way to use the rheometer and available geometries. Flow curves were measured using both a roughened bob and cup and a vane with a smooth larger cup. The yield stress was measured through two different methods: using oscillation and using a shear stress ramp where the yield stress was determined from an inflection in the angular displacement, suggesting a sudden fast movement of the bob caused by the suspension yielding. To compare these different methods, the eucalyptus MFC sample from Chapter 6 was diluted to 1.0% solids and used for both geometries for all sets of experiments. The aim of the experiments was not to find the true value of yield stress and viscosity of the MFC suspension but to find a method where the rheology of a suspension could be meaningfully compared with another since different measurement geometries have been found to show the same trends and behaviour despite not having exactly the same result.¹²⁴

One measurement geometry was a roughened cup and bob with bob diameter 25 mm and length 37.5 mm and cup diameter was 27.5 mm and the length 62.5 mm. (C25 DIN roughened SW120755 and PC DIN roughened C004555). The second measurement geometry was a vane (4V25) with a diameter of 25 mm and a length of 61 mm with a significantly larger cup with diameter 37 mm and length 66 mm. In order to use the vane with the larger cup, the size of the cup was altered from the C004555 cup in the Manage Geometries section of the rSpace software. An inertia calibration was then performed to confirm that the software had registered the change in size of the base cup. This stage was performed with the assistance of Tania Selina.

A shear rate ramp from 0.1 – 1000 s⁻¹ with a logarithmic increase and 90 samples per decade was used to analyse the samples. The ramp time was two minutes. Flow curves were measured for both geometries. Unless otherwise stated, three measurements were taken for each sample and graphs show averages with standard deviation error bars.

A stress ramp was considered as one potential method to measure yield stress. The stress was increased in a linear fashion from 0.01 to 10 Pa over 2 minutes with 200 samples and plotted against the angular displacement of the bob. The inflection point of the curve was taken as the yield stress as it represents a sudden fast movement of the sample. Three experiments were run for each geometry and the averages are plotted. Error bars represent standard deviation. Three frequency sweeps from 0.1- 50 Hz at 0.1% shear strain with 10 samples per decade on a logarithmic scale were obtained for each geometry to determine a frequency where stable readings of the elastic and viscous modulus were obtained that could be used for the amplitude sweeps. Amplitude sweeps were performed at 0.5 Hz from 0.1- 1000% shear strain with 10

samples per decade on a logarithmic scale. For oscillation experiments, data is shown as the average of 3 experiments and error bars represent standard deviation.

Figure 3.4 shows the change in viscosity when shear rate was increased from 0.1- 1000 s^{-1} for both the vane and large cup and the roughened cup and bob geometries. The viscosity is higher over the whole shear range for the vane and large cup geometry which may suggest that some measurement artefacts such as wall slip may be occurring for the roughened cup and bob geometries. However, the cup and bob geometry shows the characteristic dip followed by a small bump in viscosity at low shear rate which is often thought to be due to the formation and break down of flocculated cellulose which is not apparent in the flow curve from the vane and large cup geometry.^{60,124}

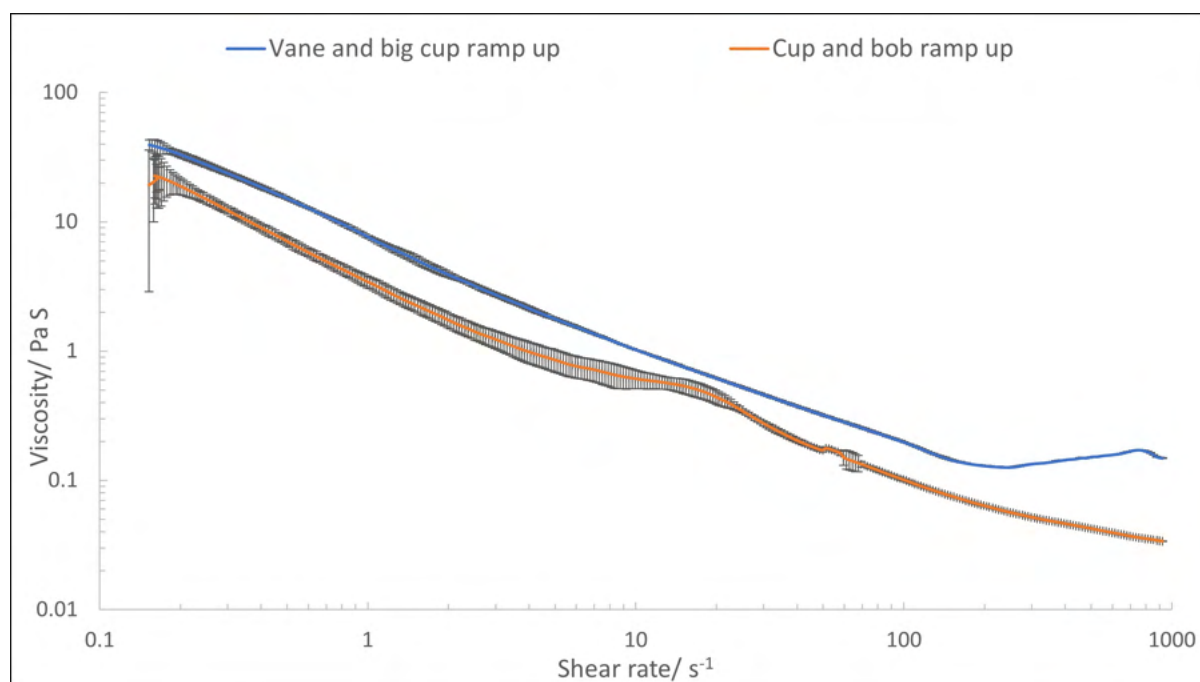


Fig. 3.4. . Shear rate ramp up for MFC at 1.0% solids using a roughened cup and bob or a vane with larger cup geometry. Data shows an average viscosity from three tests per geometry and error bars represent standard deviation.

Figure 3.5 shows how the angular displacement of the bob or vane changes as the shear stress was increased. Yield stress was determined as the inflection point in this curve as that signifies a sudden increase in movement as a result of the shear stress being high enough to overcome the yield stress. The yield stress for the cup and bob geometry was determined to be 3.5 Pa and for the cup and vane geometry 6.1 Pa. Clearly a larger yield stress value is seen for the vane geometry which may suggest that some wall slip or shear banding occurs in the cup and bob geometry which reduces the stress needed to cause a sudden movement.¹²⁵

Figure 3.6 shows data from the oscillation experiment where frequency was increased at a constant strain for the cup and bob and vane and large cup geometries respectively. The frequency of 0.5 Hz used by Schenker and co-authors for amplitude sweeps appears to fall in the linear viscoelastic range for this sample for both geometries.¹²⁴ Therefore, 0.5 Hz was chosen as the frequency to be used in the amplitude sweeps.

Figure 3.7 shows the elastic modulus (G'), viscous modulus (G'') and phase angle for the amplitude sweep at 0.5 Hz using the cup and bob or cup and vane geometry. There was some significant variation at very low values of complex shear stress for the cup and bob geometry which may have been due to the difficulty in accurately measuring small deformations at very

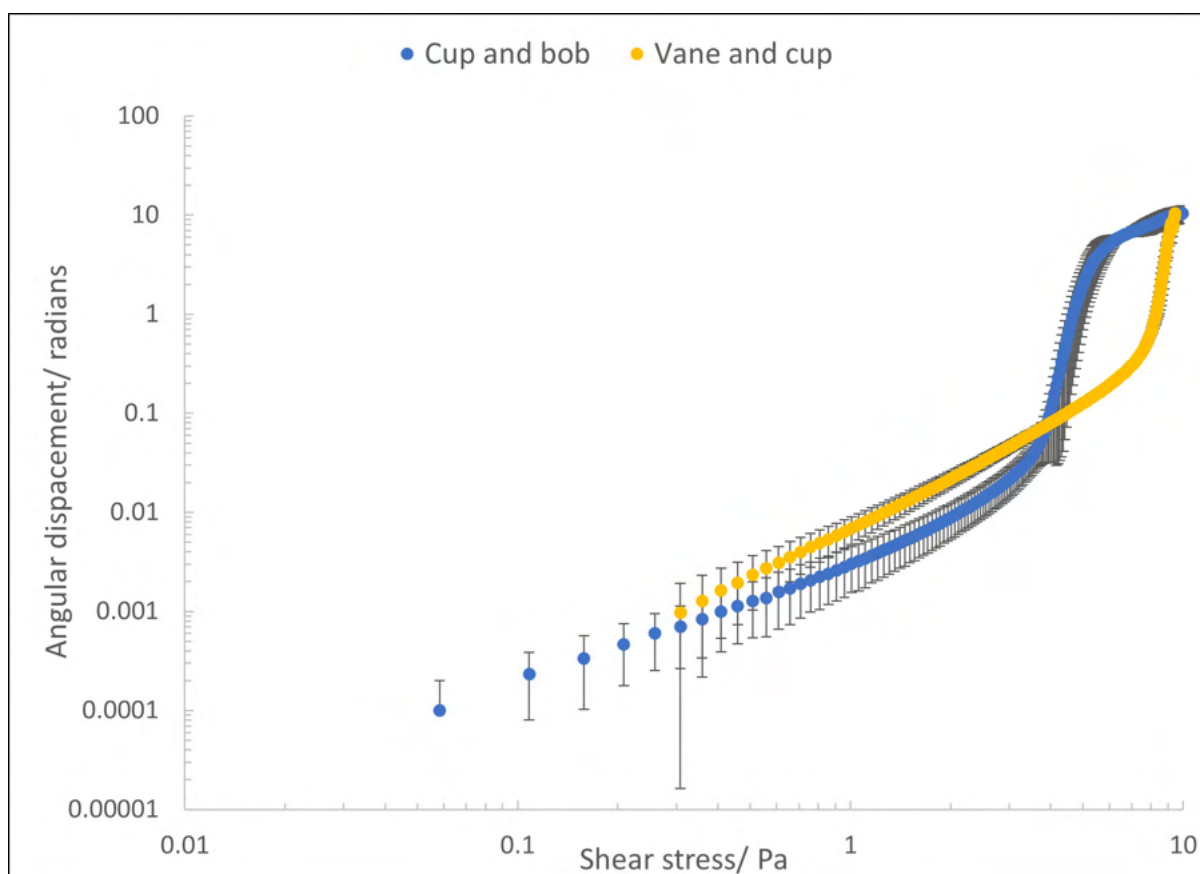


Fig. 3.5. Shear stress ramp for MFC at 1.0% solids using a roughened cup and bob or a vane with larger cup geometry. Data shows an average data from three tests per geometry and error bars represent standard deviation.

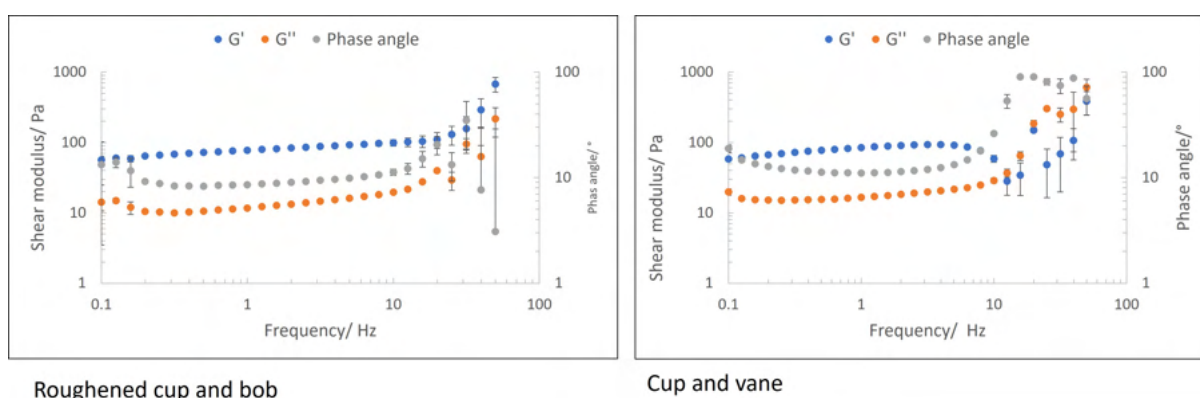


Fig. 3.6. Oscillation frequency sweep for MFC at 1.0% solids using a roughened cup and bob or a vane with larger cup geometry. Data shows an average data from three tests per geometry and error bars represent standard deviation.

Table 3.3

Table showing yield stress results from different methods of measurement

Geometry	Shear stress at 5% increase from minimum phase angle/ Pa	Shear stress at phase angle of 45°/ Pa	Shear stress at maximum product of elastic modulus and shear strain / Pa	Yield stress from stress ramp/ Pa
Cup and bob	0.28	2.76	2.71	3.50
Vane and large cup	0.28	5.90	5.07	6.10

low shear stress. Using the method by Schenker and co-authors the yield stress is defined at the shear stress where the phase angle increases from the minimum by 5%. If the minimum phase angle is defined within the stable region at a complex shear stress of 0.0237 Pa, the point where the phase angle has increased by 5% would be 0.28 Pa which is the point where the elastic modulus begins to decrease.¹²⁴ However, if using the methods described by Nazari and co-authors, the shear stress at point where the phase angle is 45 degrees is 2.76 Pa or the maximum product of shear strain and the elastic modulus is 2.71 Pa.¹²⁵ Figure shows the results for the amplitude sweep using the vane and large cup and Table 3.3 shows a summary of the yield stress calculated using the same methods for both geometries.

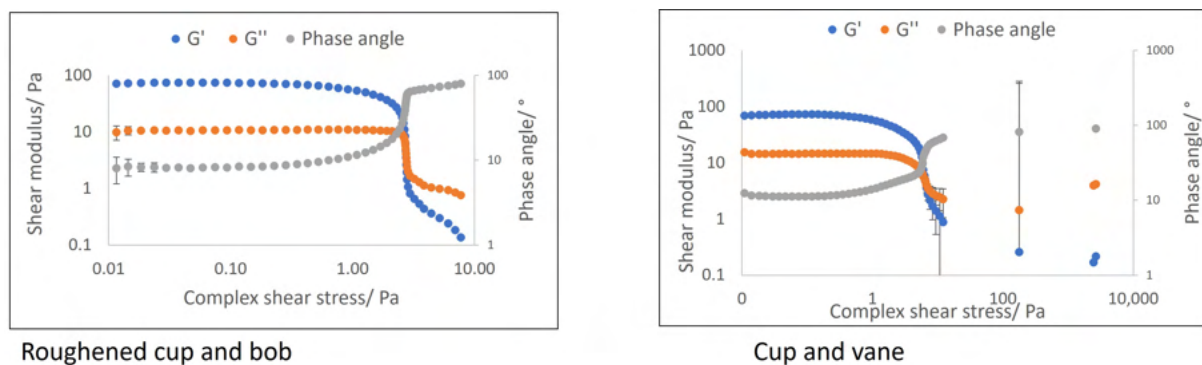


Fig. 3.7. Oscillation amplitude sweep for MFC at 1.0% solids using a roughened cup and bob or a vane with larger cup geometry. Data shows an average data from three tests per geometry and error bars represent standard deviation.

In the flow curves, a higher viscosity is seen for the vane and large cup geometry compared to the roughened cup and bob geometry which may suggest some wall slip occurred. However, the vane and large cup geometry does not show the typical shape of flow curves of MFC suspensions since there does not appear to be a dip in viscosity at low shear rates caused by the formation of flocs. Furthermore, the shear thinning behaviour stops at high shear rates for the vane geometry which is not typical for MFC flow curves.^{60,124} This irregularity could be caused by disturbances of the suspension by the vane blades or possibly the assumption that material trapped between the blades of the vane does not flow is less valid at high shear rates.^{130,131} The wide gap between vane blades and the large cup could also lead to different flow profiles within the measurement gap.¹²⁹ It is also worth noting that the cup used for the large cup in this research had a smooth surface which may have led to more measurement artefacts such as slip than was seen in research papers using a roughened or serrated large cup. The yield stress appears to depend on how it is measured. This is not uncommon and has been observed previously for measuring yield stress of MFC suspensions.¹²⁵ However, in this work,

Table 3.4

Experimental parameters chosen for the comparison of different MFC samples

Experiment	Measurement geometry	Yield stress determination
Flow curves	Roughened cup and bob	N/A
Oscillation	Roughened cup and bob	Complex shear stress when phase angle= 45°

the true value of the yield stress is less important than having a reliable method to compare the yield stress of different MFC samples. The method used by Schenker and co-authors where the yield stress is calculated from the stress at a 5% increase in phase angle gives very low values of yield stress in this work.¹²⁴ Figure 3.7 shows that there is a gradual decrease in the elastic modulus (G') beginning at approximately 0.3 Pa which explains why there is a small increase in phase angle. Measurement of yield stress at a phase angle of 45° by Nazari and co-authors give significantly higher values of yield stress for both geometries because this is assigning the yield stress as a much larger deformation than the previous measurement.¹²⁵ This determination of yield stress may therefore be more useful in comparing different samples. In this case, there is a large difference between the vane and bob geometries with the vane geometry showing a much higher yield stress. This suggests that artefacts such as wall slip or shear banding may be occurring in the cup and bob geometry.¹²⁴ Supporting this, the yield stress value measured from the stress ramp is also significantly higher for the vane geometry than the cup and bob. However, the standard deviations for the shear stress ramp method were significantly higher than the oscillation methods which can be seen as large error bars on the graphs. The oscillation data also gives more information about the material such as the elastic and viscous modulus which could be useful for characterization of the MFC. For this reason, the oscillation experiments may be a better option than the shear stress ramp. In the oscillation experiments, the vane geometry showed higher standard deviations than the cup and bob geometry. There was also a more gradual change in the elastic and viscous moduli which could be another reason why the measured yield stress was higher. This gradual change may make it more difficult to distinguish easily between samples. Furthermore, the vane geometry may be less susceptible to artefacts such as wall slip but it is necessary to assume for the experiment that the material trapped between vane blades does not flow and the flow profile in the large cup is uniform which may not always be the case.^{128–130} The experimental parameters chosen to compare different MFC samples at a constant solids are shown in Table 3.4.

3.7 | Paper Testing Methods

All samples were equilibrated at 50% relative humidity (relative humidity (RH)) and 23°C for a minimum of 15 hours before testing in a climate controlled room. All paper testing with the exception of Kit and HVTR testing, which for safety reasons were performed in a fume cupboard, was performed within these testing conditions.

3.7.1 Grammage

Sheets were weighed on a four decimal place analytical balance. Mass was divided by sheet area to calculate the grammage. Each individual sheet made per set of sheets was weighed and an average and standard error was calculated.

3.7.2 Thickness

Paper thickness was measured using a Messmer digital micrometer. This method of thickness measurement determines height between two parallel plates. Therefore, it potentially overestimates the thickness of paper as surface roughness effects in the paper will make the sheets appear thicker than they are and the pressure may lead to some compression.¹²² Despite this, the method of thickness measurement through digital micrometer is rapid and can easily be performed at 50% RH and 23°C without requiring any complex sample preparation methods. The resolution of the instrument was 1 μm and the pressure between the plates was 1000 ± 10 kPa.¹³² The area of the measurement plates was 0.05 m². 10 thickness measurements were taken per set of sheets and an average and standard error was calculated.

3.7.3 Air permeability

Bendtsen porosity is a measure of air permeability in which air is forced through a paper sample under pressure and the pressure difference across the paper is recorded. This method detects only pores which connect across the thickness of the paper.¹²² Bendtsen porosity was measured using a Parker Print Surf roughness tester Model 58-07-00 Twinhead machine modified with a permeance sensing head. A clamping pressure of 2000 kPa was used. The resolution of the instrument was 1 mL min⁻¹. A minimum of 5 measurements were taken per set of sheets and an average and standard error were calculated.

3.7.4 PPS Roughness

PPS roughness was measured using an M594 Parker Print Surf Messmer Büchel roughness tester. PPS roughness is a measurement of leakage of air between a rubber gasket and a paper surface under pressure. A rougher paper surface leads to more air leakage around the seal, the air leakage is then measured as the roughness.¹³³ A minimum of 5 PPS roughness measurements were taken per sample and the average and standard error were calculated. Clamping pressure used was 1000 kPa.

3.8 | Measurement of Optical Properties of MFC Films and Coatings

When light interacts with an interface where there is a change in refractive index, there are several different occurrences:

- Some of the light is reflected from the surface, either in a specular manner or diffusely due to surface roughness.
- The remaining light is refracted and enters the sheet.
- Some of the refracted light is absorbed.
- The remaining refracted light is scattered and can then be transmitted through the layer or reflected back from the surface.¹³⁴

In a sheet of cellulose, absorption could occur through chromophores in lignin. This effect is what gives unbleached cellulose a yellow or brown colour. In bleached pulp, the absorption coefficient is low. Absorption is a function of the chemical properties or energy levels of a material and does not usually depend on the physical structure of a material.^{135,136}

In cellulose networks, light is scattered at fibre surfaces. Because of this, differences in the scattering coefficient of paper relate to differences in the unbonded cellulose surface area. A cellulose network with very low porosity will have a lower scattering coefficient than a cellulose network with high porosity and therefore a greater area of unbonded fibre.¹³⁵

3.8.1 The Kubelka- Munk Approximation

The Kubelka- Munk approximation was used to calculate the scattering coefficient of MFC films and coatings from diffuse reflectance measurements. The Kubelka-Munk approximation is shown in Equation 3.2, where K is the absorption coefficient, S is the scattering coefficient, and R_∞ is the diffuse reflectance of an infinitely thick layer of material.¹³⁷

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (3.2)$$

The parameter a can be expressed in terms of R_∞ in Equation 3.3 and an additional parameter b can be used to help further simplify the Kubelka-Munk equations. as shown in Equation 3.4 and 3.5.¹³⁷

$$a = \frac{1}{2} \left(\frac{1}{R_\infty} + R_\infty \right) = \sqrt{b^2 + 1} \quad (3.3)$$

$$b = \frac{1}{2} \left(\frac{1}{R_\infty} - R_\infty \right) = \sqrt{a^2 - 1} \quad (3.4)$$

$$R_\infty = a - b \quad (3.5)$$

The Kubelka-Munk approximation can also be expressed by Equation 3.6 where R_g is the reflectance of the background, w is the grammage of the sheet, and R is the measured reflectance of the layer.¹³⁷

$$\ln \frac{(R - \frac{1}{R_\infty})(R_g - R_\infty)}{(R_g - \frac{1}{R_\infty})(R - R_\infty)} = Sw \left(\frac{1}{R_\infty} - R_\infty \right) \quad (3.6)$$

For experimental measurements of S and K , the parameter R_0 can be used where R_0 describes the measured reflectance of a layer of material over a black background where $R_g = 0$. Using these simplifications, S can be calculated when the grammage is known from measurements of R_0 and R_∞ using Equation 3.7.¹³⁷

$$\ln \frac{1 - R_0 R_\infty}{1 - \frac{R_0}{R_\infty}} = Sw \left(\frac{1}{R_\infty} - R_\infty \right) \quad (3.7)$$

3.8.2 Assumptions of the Kubelka- Munk Approximation

Use of the Kubelka-Munk approximation operates under the following assumptions:^{135–137}

- The measurements must take place under diffuse illumination- this means that the angular distribution of the illuminating light must be isotropic.
- There is no significant specular reflection from the surface.
- Scattering particles are smaller than the layer thickness.
- Scattering particles should be distributed randomly and homogeneously throughout the layer thickness so that S and K are the same throughout.

In addition to the above assumptions, in order to measure S and K , there should be a measurable contrast between the reflectance of the layer over a non reflecting background R_0 and the reflectance of an infinitely thick layer of the material R_∞ .¹³⁵

3.8.3 Measurement of Light Scattering Coefficient of MFC Films

The MFC films produced in the laboratory were translucent and it was not possible to achieve an opaque stack of films. Therefore, an alternative method was required to calculate S without having a direct measurement of R_∞ . Equation 3.8 was used to calculate a from two experimental measurements of reflection. R_0 is the reflectance of an MFC film over a black background, R is the measured reflectance of an MFC film over a reflecting background and R_g is the reflectance of the background.¹³⁷ Therefore, two measurements were made. One was an MFC film over a black background (R_0) and the other was the reflectance of an MFC film over a stack of 80 g m⁻² white copy paper (R). The final constant measurement was the R_∞ of the stack of copy paper which provided R_g .

$$a = \frac{1}{2} \left(R + \frac{R_0 - R + R_g}{R_0 R_g} \right) \quad (3.8)$$

Once a was calculated, b could be calculated using Equation 3.4, followed by the calculation of R_∞ using Equation 3.5; S using Equation 3.7 and the grammage of the MFC film as w ; and K using Equation 3.2.

3.8.4 Measurement of Light Scattering Coefficient of MFC Coatings

Measurement of the light scattering coefficient of thin MFC coatings applied via vacuum filtration to a base paper is more complex than MFC films because neither a direct measurement of R_0 or R_∞ is possible. To achieve this, a discrete layer of MFC coating was assumed; measured over the top of two different bases. The first measurement was taken of the MFC coated sheet over a black background, therefore using a background of R_0 of the base sheet. The second reflectance measurement was the MFC coated sheet over an opaque stack of base papers made by filtering water through the base paper and drying in the same method as the MFC coated papers. Therefore, the background reflectance for the second measurement was the R_∞ of the base sheet.

The intention of the experiment was to measure S and K of MFC coatings. This was achieved using simultaneous equations with Equation 3.8.¹³⁷ Since the parameter a is a function of R_∞ which is a constant property of the MFC coating in both measurements, Equation 3.9 was derived to calculate the R_0 of the MFC coating. R_1 is the measured reflectance of the MFC coated sheet over the black background; R_{g1} is the R_0 of the base sheet; R_2 is the measured reflectance of the MFC coated sheet over an opaque stack of base sheets; and R_{g2} is the R_∞ of the base sheet. Simplification of Equation 3.9 led to Equation 3.10 which allowed calculation of R_0 for the MFC coating. Following this, Equation 3.8 was used to calculate a ; 3.4 was used to calculate b ; 3.5 was used to calculate R_∞ ; and 3.7 and the grammage of the MFC coating was used to calculate S . Other authors have described ways to calculate the optical properties of coated papers using the Kubelka-Munk approximation.^{138–140}

$$\frac{1}{2} \left(R_1 + \frac{R_0 - R_1 + R_{g1}}{R_0 R_{g1}} \right) = \frac{1}{2} \left(R_2 + \frac{R_0 - R_2 + R_{g2}}{R_0 R_{g2}} \right) \quad (3.9)$$

$$R_0 = \frac{R_1 R_{g2} - R_2 R_{g1}}{R_{g1} R_{g2} R_1 - R_{g1} R_{g2} R_2 - R_{g1} + R_{g2}} \quad (3.10)$$

A Datacolour Elrepho 3000 was used to measure the light scattering coefficient of MFC films and coatings in a wavelength range of 420- 700 nm in steps of 10 nm using a D65 illuminant. A minimum of 6 measurements of reflectance over each background were taken for each type of MFC film or coating. S was calculated for each wavelength using a program written in Python (see Appendix).

3.8.5 Use of Kubelka Munk Scattering Coefficient to Calculate a Comparative Scattering Particle Size Parameter

Kortüm and co-workers found that the Kubelka-Munk scattering coefficient was inversely proportional to particle size of glass filters at a constant wavelength. In addition, there was a decrease in scattering coefficient with increasing wavelength for particles with an average particle size smaller than 1.5 μm .¹⁴¹

Rayleigh scattering describes scattering from a single particle smaller than the wavelength of light. For spherical particles with diameter d , Equation 3.11 describes Rayleigh scattering where I is the intensity of the scattered light, I_0 is the intensity of the incident light, θ is the scattering angle, λ is the wavelength of the incident light, n is the refractive index of the particle and s is the distance of the particle from the detector. Equation 3.11 shows that the intensity of the scattered light is proportional to λ^{-4} .¹³⁴

$$I = I_0 \left(\frac{1 + \cos^2 \theta}{2s^2} \right) \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{n^2 - 1}{n^2 + 1} \right)^2 \left(\frac{d}{2} \right)^6 \quad (3.11)$$

Kortüm and Oelkrug plotted the logarithm of the Kubelka-Munk scattering coefficient against the logarithm of the measurement wavenumber for particles with an average particle size between 0.1 and 0.01 μm . The gradient of the resulting straight lines were measured. For smaller particle sizes, a steeper gradient was observed. For larger particles with diameters 0.1- 0.4 μm , the gradient of the lines was approximately -1. For particles much larger than the wavelength of light, there was no effect of wavelength on S .^{137,142} Gate found that for particles sized between 0.5 - 2 μm , plots of $\text{Log}S$ as a function of $\text{Log}\lambda$ had gradient between -1 and -0.67.¹⁴³

Equation 3.11 can be simplified for a system with a constant s , θ , n and d to Equation 3.12 where S_R is the intensity of Rayleigh scattering and k is a constant describing the terms in Equation 3.11. Equation 3.12 can also be written in a logarithmic form shown in Equation 3.13.¹⁴⁴

$$S_R = k\lambda^{-4} \quad (3.12)$$

$$\log_{10} S_R = \log_{10} k - 4\log_{10} \lambda \quad (3.13)$$

Equation 3.12 shows that the intensity of Rayleigh scattering is proportional to the negative fourth power of the wavelength. Using Equation 3.13, a plot of $\log_{10} S$ as a function of $\log_{10} \lambda$ can be created for Kubelka Munk scattering coefficient data over a wavelength range if it is assumed that the Kubelka Munk scattering coefficient is proportional to the Rayleigh scattering intensity. Therefore, the magnitude of the gradient of a plot of $\log_{10} S$ as a function of $\log_{10} \lambda$ can give a comparative measure of scattering particle size between different samples provided that the refractive index remains the same. This is because the dependence on wavelength may give an indication of the degree of Rayleigh scattering occurring and Rayleigh scattering only occurs for particles smaller than the wavelength of light. A gradient closer to -4 suggests a smaller scattering particle size because there is a wavelength dependence similar to that

seen in the Rayleigh equation.¹³⁷ The magnitude of the gradient is known as the wavelength exponent.¹⁴⁴

In the present thesis, the wavelength exponent of MFC films and coatings was calculated from the Kubelka Munk scattering coefficient over a visible light wavelength range (420- 700 nm). A minimum of six measurements were taken per sample and the average and standard error of the wavelength exponent was calculated for each sample where a linear dependence was observed. This analysis was performed using a Python script (see Appendix).

3.9 | Mercury Intrusion Porosimetry on MFC Films

Liquid mercury is non wetting on most solid surfaces due to a very high surface tension. A mercury porosimetry experiment is performed by forcing mercury into pores in a sample through application of high hydrostatic pressure. This pressure increase is performed in steps so that mercury can enter into smaller and smaller pores in the sample. Pore diameter and pressure for cylindrical pores are linked through the Washburn equation (Equation 3.14) where d is pore diameter, γ is surface tension of mercury, p is applied pressure and θ is mercury contact angle.¹⁴⁵

$$d = \frac{-4\gamma}{p} \cos\theta \quad (3.14)$$

During the porosimetry experiment, intruded mercury volume is measured as a function of pressure. This provides a cumulative pore volume as a function of pore diameter. Measurements are taken for both the pressure increase and decrease. A hysteresis effect is generally observed where some mercury remains trapped in the sample and is not expelled from pores when pressure decreases.¹⁴⁵

Mercury intrusion porosimetry is a useful tool to compare pore size distributions of samples; however, the pore size measured by porosimetry relates to the size of the entrance to the pore not to the body of the pore. This means if a pore has a narrow entrance but is large inside, it will be recorded as a low diameter pore because high pressure was required to intrude mercury into the narrow opening. Similarly, the porosimetry analysis assumes cylindrical pores and it is likely that in reality pore geometries will be complex and irregular. Furthermore, the high pressures required to intrude mercury may damage the sample, leading to errors in the results.^{145,146}

In this thesis, mercury porosimetry was performed using two Thermofischer Scientific Pascal porosimeters 140 and 240. SOLIDS software was used to perform and monitor the experiments and to produce data for the measurement of relative and cumulative pore volume as a function of pore diameter. A mercury contact angle of 140° was used in pore size calculations. This is a standard mercury contact angle used for porosimetry experiments.¹⁴⁵

The experiment was performed by cutting an MFC film with scissors to a mass between 0.15- 0.25 g, folding the film and placing it into a glass dilatometer. The sample was clamped into the low pressure machine and left to run. Following this, the dilatometer containing the sample was removed, placed into the autoclave on the high pressure machine and left to run. Pressure was increased from 0.0147 MPa to 180 MPa during the test. The pressure increase was done in "Pascal" mode with an increase speed between 3-7 MPa/minute and pressure decrease was performed in continuous mode with a speed between 8-24 MPa/minute. The difference in methods for pressure increase and decrease is due to only the pressure increase data being used to calculate pore size distributions. Mercury porosimetry data was extracted from the SOLIDS software and the Pore Size and Specific Pore Volume calculated by the software was

transferred to a data smoothing program made by Tony Hiorns at Imerys Minerals Ltd to produce smooth curves of cumulative pore volume and a pore size distribution.

Used mercury was recycled through the use of a separating funnel to separate mercury from the hydraulic oil used in the high pressure machine. The mercury is periodically cleaned using hexane in a separating funnel by the equipment manager.

3.10 | Crystallinity Index of Cellulose Sheets

3.10.1 Crystallinity Measurements for Cellulose

Different crystalline forms of cellulose exist but cellulose I is the predominant form found in nature. Cellulose contains both crystalline and amorphous material; the crystallinity index of cellulose is a parameter describing the amount of crystalline material relative to amorphous material⁵⁷.

Crystallinity index of cellulose (CrI) can be calculated from X-ray diffraction (XRD) data using the Segal method.^{57,147} Segal and co-workers found when crystalline cotton cellulose was degraded in crystallinity through ball milling, the intensity of peaks at $2\theta = 14.4, 16$ and 22.8° (I_{002}) decreased and the intensity of the signal at $2\theta = 18^\circ$ —referred to as the amorphous intensity by the authors (I_{am})— increased. For the cellulose sample with heavily degraded crystallinity, the diffraction pattern devolved into one broad peak. The authors suggested Equation 3.15 as a quantitative measure of the crystallinity index of cellulose (CrI) based of the X-ray diffraction pattern.¹⁴⁷

$$CrI = 100 \times \frac{(I_{002} - I_{am})}{I_{002}} \quad (3.15)$$

Park and co-authors argued that the Segal method is a useful and fast way to compare samples but may not give accurate values of the crystallinity index due to underestimation of the amorphous content, considering only peak height and not area and consideration of only one crystalline peak.⁵⁷

Ruland devised a method to calculate the crystallinity index of polypropylene and nylon by calculating contribution from amorphous regions of the polymer.^{148,149} This method was later developed to apply more generally and simplified by Vonk.¹⁵⁰ Practically, this analysis requires measurement of an amorphous standard and subtracting the amorphous contribution from the crystalline trace. Lignin can be used as an amorphous standard for cellulose. A scaling factor is then applied to ensure that the amorphous curve is below the minima of the cellulose traces.¹⁵¹

Thygesen and co-authors argued that the Ruland-Vonk crystallinity of cellulose is simple to measure experimentally but requires selection of an amorphous standard and scaling of the trace of the amorphous standard which can be subjective.¹⁵¹

3.10.2 Experimental Details

X-ray Diffraction (XRD) was used to measure the crystallinity index of cellulose films- both from pulp and MFC. Films were chosen as the preferred samples to analyse because they were made of thick (50 g m^{-2}) layers and there would not be an issue of interference from the base paper as may occur if an MFC coated sample was used. In addition, films of MFC made through vacuum filtration were measured for crystallinity index because this is the form of the MFC coating so the crystal form of the cellulose in this structure is what will be relevant to the barrier properties. Guar gum from Special Ingredients was used as the amorphous standard for cellulose.

A diffraction pattern was measured from the surface of the film. XRD was performed at the University of Birmingham in the Chemistry department by the XRD facility managers using a Bruker D8 Advanced powder diffractometer with a Cu radiation target. 6 scans were performed on each sample from 2θ 5-50° with a step size of 0.02°. CrystalDiffract software from CrystalMaker software Ltd (www.crystallmaker.com) was used to analyse the results.

3.11 | Additional Characterisation Methods for MFC Coated Sheets or MFC Films

3.11.1 Optical microscopy

MFC films were imaged using a VHX-1000 multiscan Keyence digital optical microscope in reflectance mode.

3.11.2 Laser Profilometry

An interferometric laser profilometer was used to obtain a height profile image of base and MFC coated papers. A square image with width 1024 μm is produced with a 2 μm resolution in the xy plane. The machine works by scanning a 1024 μm strip of the sheet, moving 2 μm and repeating the scan.¹⁵² The images are automatically saved as csv files which can then be computed into images with coherent height profile scales using an Analysis program developed by IMERYs. The equipment is shown in Figure 3.8.

3.11.3 SEM

Scanning electron microscopy (SEM) images of coated sheets were provided by the IMERYs Minerals Ltd. microscopy department in Par, Cornwall. The sample was attached to a 45° tilted stub using silver conductive tape and carbon adhesive. A Pt layer was sputter coated onto the surface. A further 25° tilt was then added once the sample was positioned in the microscope. Secondary electron images were produced using a Jeol 6700 field emission electron microscope. For visualisation of cross sections of sheets, samples were cured in an epoxy resin, and cut with an Ultramicrotome with glass followed by diamond.

3.11.4 Coating Formation

An Epsom V500 Photo Scanner and the Epsom scanner software were used to visualise MFC coated sheets. To visualise the visible flocculation patterns in MFC coatings, the scanner was used in Reflective mode.

3.11.5 Moisture Content of MFC Films

Moisture content of MFC films at 50%RH and 23°C was measured using 5 cm² circles of MFC films. 4 discs were cut from each set of films. The MFC films were conditioned for 24 hours at 50%RH and 23°C before weighing on a 4 decimal place analytical balance. Following this, the MFC film discs were oven dried at 100°C for 1 hour and then re-weighed. Moisture content at 50%RH and 23°C was calculated as the percentage difference in mass between oven dried and equilibrated sheets. Average values and standard error were calculated.

3.11.6 Water Contact Angle

Water Contact Angle Water contact angle was measured on 15 mm wide strips of MFC films cut using a guillotine. Distilled water was used for the measurement. Water contact angle

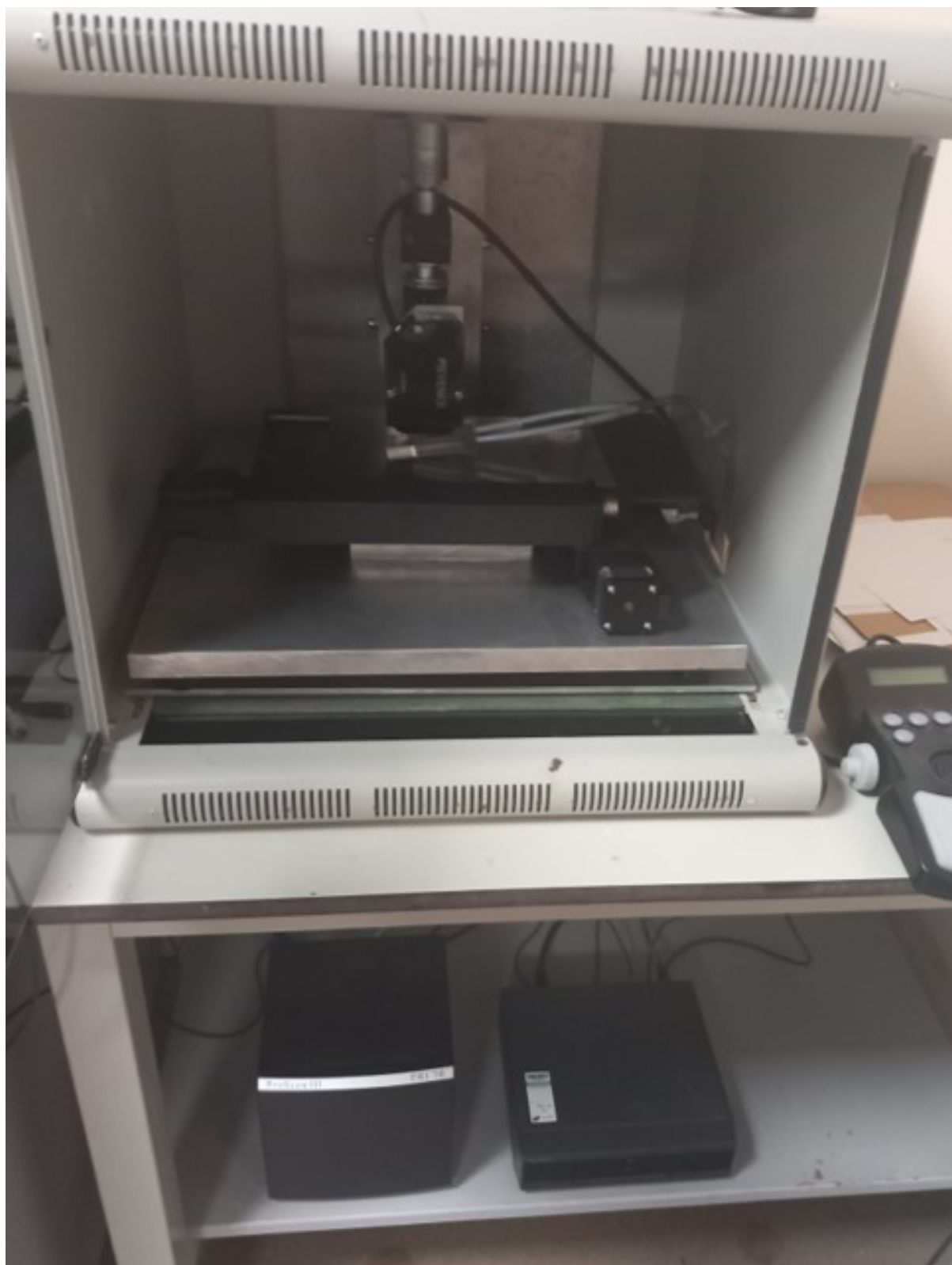


Fig. 3.8. Interferometric laser profilometer used to measure height profiles of MFC coated paper and MFC films

was measured using an RDM Test Equipment Fibro 1100 DAT. Distilled water was drawn into a 1 mL syringe with capillary tubing attached. The sample was attached to the machine measurement bar using double sided tape. DAT-Gig E software was used to control the

machine and measure water contact angle. A minimum of 5 drops of water were recorded per MFC film. The water drop size was 4 μL and the drop was monitored for 60 seconds.

3.11.7 Fourier Transform InfraRed (FTIR) Spectroscopy of MFC Films

FTIR was used to gather information on chemical composition of MFC films. A ThermoScientific Nicolet is50 FT-IR spectrometer was used in Attenuated Total Reflection (ATR) mode. The MFC film was placed onto an ATR crystal and clamped down with an anvil. 32 scans were recorded between 400 - 4000 cm^{-1} with a resolution of 4 cm^{-1} . OMNIC software was used to collect and process the spectroscopic data.

Nelson and O'Connor calculated crystallinity index of cellulose from infrared spectra using two ratio of absorption intensities shown in Equation 3.16 and Equation 3.17 and showed that the crystallinity index was proportional to that calculated from XRD data using the Segal method.^{153,154}

$$CrI_{IR1} = \frac{A_{1429\text{cm}^{-1}}}{A_{893\text{cm}^{-1}}} \quad (3.16)$$

$$CrI_{IR2} = \frac{A_{1372\text{cm}^{-1}}}{A_{2900\text{cm}^{-1}}} \quad (3.17)$$

In this thesis, Equation 3.16 and Equation 3.17 were used to calculate crystallinity indices of MFC films on FTIR spectra collected through ATR mode.

3.11.8 Pycnometry

In Chapter 6, an Accupyc II 1340 V2.01 pycnometer is used to measure the density of MFC films. To do this, MFC films were rolled into tubes and then folded so that they fit into the testing chamber with a cell volume of 11.7220 cm^3 . Nitrogen was used as the testing gas with 10 purge cycles.

3.12 | Barrier Testing Methods

3.12.1 Water vapour transmission rate (water vapour transmission rate (WVTR))

WVTR was measured using 68-3000 EZ- Cup Vapometer Permeability Cups from Thwing-Albert Instrument Company. These are cylindrical aluminium pots which allows a 3 inch diameter circle of paper to held above an empty chamber. Merck Supelco 1.3 mm silica gel with orange indicator was oven dried in a shallow metal dish at 130°C until the colour changed from white to dark orange throughout, indicating the material was dry. Dried silica gel (30 g) was placed in the base of a permeability cup to create a zero humidity environment, the paper was clamped over the top of the cup and the cup was placed in a 50% RH, 23°C room. Due to the difference in RH from the controlled atmosphere room to the cup filled with dry silica gel, water vapour diffuses into the cup and is absorbed by the silica gel. This is monitored by weighing the pots at regular time intervals to record the rate of increase in mass. The area of exposed paper or film in the cup is 0.0032 m^2 . The final WVTR value is calculated using Equation 3.18 where Area is the area of exposed sample and dm/dt is the rate of mass change in the pot over time. An example of one of the permeability pots is shown in Figure 3.9.

$$WVTR(gm^{-2}day^{-1}) = \frac{24 * (dm/dt)(ghour^{-1})}{Area(m^2)} \quad (3.18)$$



Fig. 3.9. Example of a permeability pot used to measure WVTR. Film or paper sample is screwed into place between rubber gaskets above an empty chamber.

To use this WVTR measurement on paper or film samples, they must be cut to 3 inch diameter circles. This was achieved using a UCEC 3 inch circle diameter paper hole punch. MFC film samples were too fragile for cutting using this method so a template was cut out and used to cut the MFC films with scissors.

Initially, the experimental method used in Fiberlean Technologies was to put 30 g silica gel into the base of the cup and weigh the pot once a day for 72 hours. This resulted in a large air gap of 4.2 cm between the top of the silica gel and the paper sample. Additionally, over the course of the 72 hours, there would be a decrease in how much mass was gained over time- particularly for paper samples which were highly permeable to water vapour.

Gennadios and co-workers suggested that for films with a relatively high WVTR- such as those made from polysaccharides like cellulose- the cup method may lead to an underestimation of WVTR. This is because transmission rate through the film is relatively high, leading to a layer of air with a high concentration of water vapour in the cup, therefore increasing the RH inside the cup and reducing the concentration gradient from the outside.¹⁵⁵ Schultz and co-authors

found that when the air space in the cup between the film and the salt controlling RH inside the cup was increased, there was a decrease in WVTR measured. This method uses the same principle of a water vapour concentration gradient but RH inside the cup is controlled by salt solution rather than a desiccant and the cups were placed in a desiccator so that water vapour diffused out of the cup.¹⁵⁶ Hu and co-workers also found that increasing the air gap between a film and distilled water in a cup decreased the measured value of WVTR due to a reduced RH in the air gap. The authors suggested that for water vapour permeable films when water is placed inside the cup, the rate of water vapour transmission through the films may be greater than the rate of evaporation and diffusion of water vapour to the film surface.¹⁵⁷ This effect was also seen by McHugh and co-authors.¹⁵⁸ A similar effect may occur with the silica gel—potentially the rate of diffusion to and absorption by the silica gel is slower than the rate of water vapour transmission through the film, therefore leading to increased RH and a slower rate of diffusion of water vapour into the cup.

To improve the WVTR measurement, the gap between the silica gel and paper sample was decreased. Ideally, this would be done by increasing the amount of silica gel until just below the surface of the paper but this technique made the pots too heavy for the analytical balance. As a result, 3 inch diameter aluminium dishes were stacked inside the cup to raise the height of the silica gel. The mass of dry silica gel was kept constant at 30 g. The commercial copy paper, which was used as a base for barrier coating in this research project, was used as an example of a highly water vapour permeable paper to test improvements to the WVTR method. Figure 3.10 clearly shows that decreasing the gap height between the silica gel surface and the paper increases measured WVTR. Figure 3.10 shows that for high permeability samples even a 1 cm gap may lead to some measurement error due to increased water vapour concentration in the gap. Therefore, it was decided that a method of stacking three aluminium dishes inside the permeability pot to raise the height of the silica gel and decrease size of the air gap to 1 cm would be used in the project.

As well as reducing the air gap, the timing of the experiment was changed. Previously, the pots were weighed once a day for 72 hours. To improve the test, when 49 g m^{-2} sheets made from an unrefined NBSK pulp—which highly permeable to water—were tested, the experiment was modified to weigh the pots more frequently. This provided a plot of mass of pot as a function of time shown in Figure 3.11. This data shows that there is a decrease in mass gain of the pots over the course of the WVTR experiment. Therefore, it was decided to record mass of pots as a function of time over the course of 48 hours. The graph would be consulted to avoid including the plateaued data in the final result. This plateau effect could be due to saturation of the top layer of silica gel, which was observed in the experiments as a layer of white silica gel on top of a layer of dark orange, dry silica gel. This may lead to increased RH inside the pot and therefore slow diffusion similar to that suggested by other authors.^{155–158}

The final method used to measure WVTR of paper samples and cellulose films was to stack three aluminium dishes in the base of the permeability pot, place 30 g of oven dried silica gel on top and then clamp the paper or MFC film. This led to an air gap of approximately 1cm. The pots were left for one hour to reach an equilibrium rate of mass gain over time and then weighed at 2 hour intervals (excluding overnight) over the course of 48 hours. A plot of mass of pot as a function of time was used to determine the time period with a linear increase of mass so that plateaued regions were not included in the rate calculation.

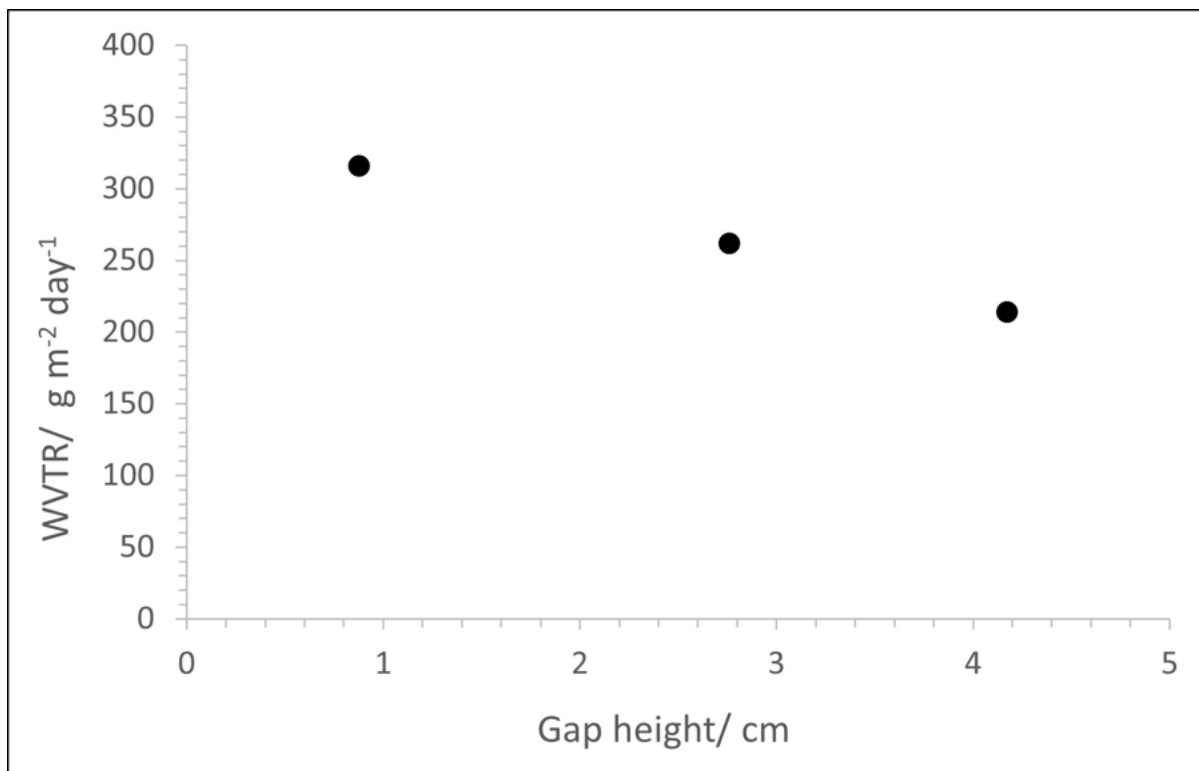


Fig. 3.10. Measurement of WVTR of Suzano woodfree paper with changing gap height between silica gel and paper. Points are the average of three measurements and standard error bars are presented.

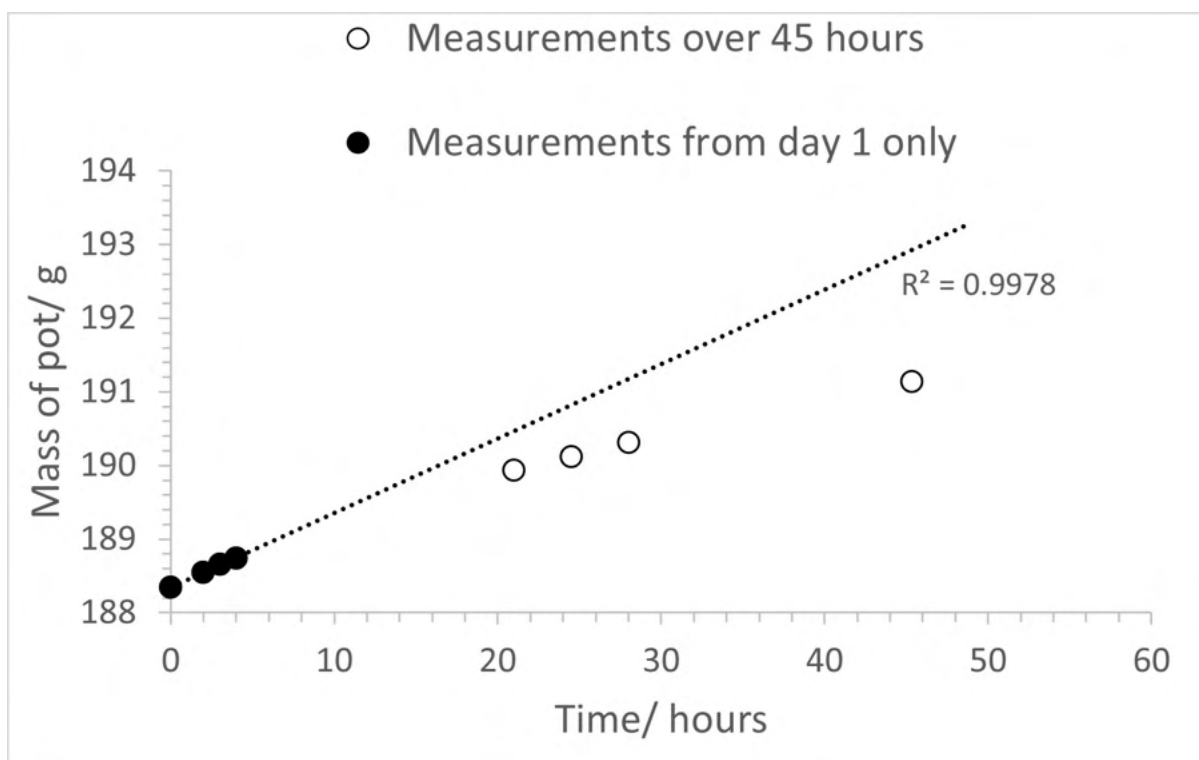


Fig. 3.11. Mass of WVTR pot with sheet made from unrefined NBSK pulp at 50 gsm during WVTR experiment. Trendline shows continuation of WVTR from first day.

3.12.2 Heptane vapour transmission rate (Heptane vapour transmission rate (HVTR))

HVTR was measured in a similar way to WVTR. Different permeability cups were used for HVTR and WVTR measurements as it was preferred to keep the heptane contaminated pots separate.

HVTR was measured inside a ventilated work station in a room conditioned at 50% RH and 23°C. The use of the extraction system may have meant that the environmental conditions above the pots were not the ideal RH and temperature, however, it was a necessary safety precaution. The sample diameter required was the same as for the WVTR test so the same cutting method was used to produce the 3-inch diameter circles.

To measure HVTR, 8 mL of n-heptane (Thermofisher Scientific) was poured into the base of a permeability pot, the paper was placed between two rubber gaskets and the lid was placed onto the pot and secured with thumbscrews. All pots were set up and then left to equilibrate for 30 minutes before weighing on a 4 decimal place analytical balance. The pots were then weighed at 2 hour intervals over the course of 6 hours to produce 4 data points of mass of the pot as a function of time. Over time, heptane evaporated from the pots due to a concentration gradient which resulted in a decrease in mass. The rate of change of mass over time along with the area of exposed sample (0.0031 m^2), was used to calculate the HVTR using Equation 3.18. Figure 3.12 shows a schematic diagram for the experimental set up of WVTR and HVTR tests.

For discussion on accuracy range of the HVTR test, see Chapter 4. Each sample was tested in triplicate unless stated otherwise and an average and standard error were calculated for each sample.

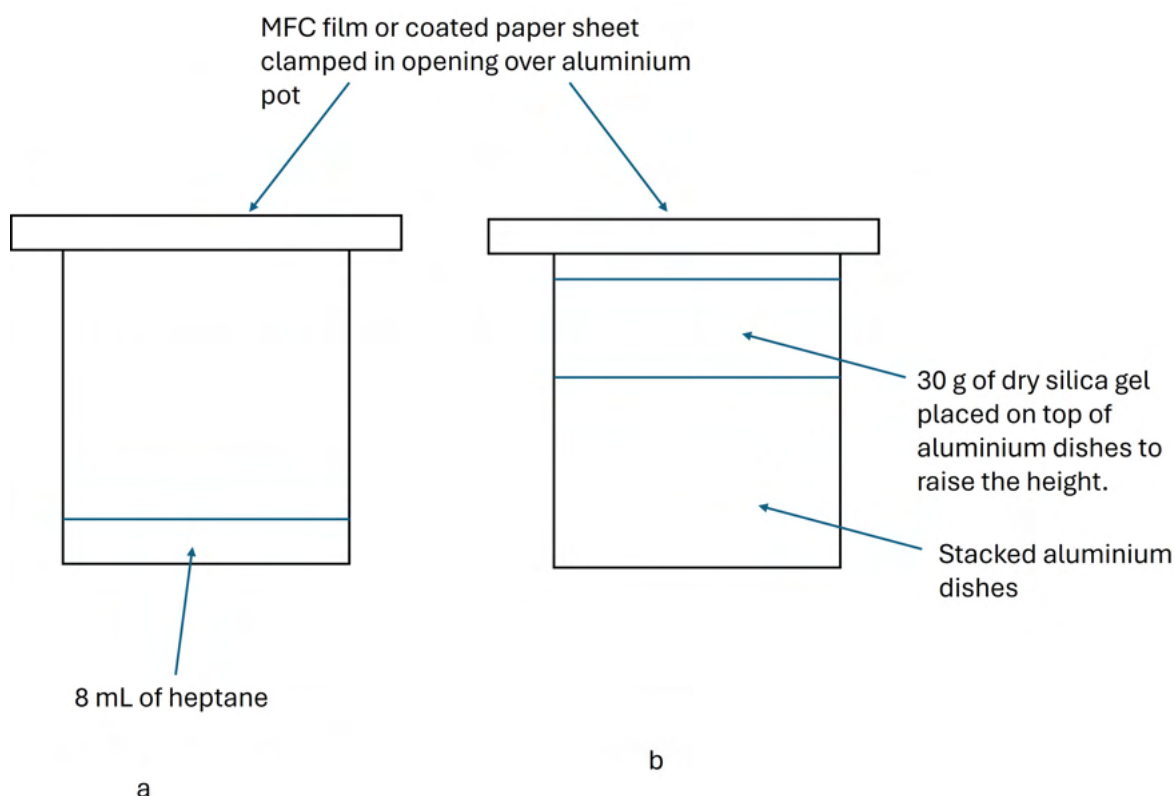


Fig. 3.12. Schematic diagram showing the experimental set up for a) WVTR and b) HVTR testing.

3.12.3 Kit Testing

Grease resistance was measured using the Kit Test (TAPPI T559 cm-12).¹⁵⁹ The Kit Test uses 12 solutions with decreasing viscosity and decreasing surface tension and therefore and increasing ability to penetrate into paper and board¹⁶⁰. Kit solution number 1 is pure castor oil, as the Kit solution number increases, the ratios of heptane and toluene increase relative to castor oil, until solution 12 which is 45 vol% toluene and 55 vol% heptane.¹⁵⁹ In this research project, further solutions with increasing proportion of heptane relative to toluene were used up to number 16 which was pure heptane. This was the testing method adopted by Fiberlean Technologies and was used so that extra data on grease resistance could be gathered. Solution composition by volume percent is shown in Table 3.5. Kit solutions were made up from their constituent components using the compositions in Table 3.5 using castor oil, heptane and toluene purchased from SigmaAldrich.

Samples were conditioned at 23°C and 50% RH for a minimum of 15 hours before testing. The testing was performed in an enclosed fume cupboard as a safety precaution. A plastic pipette was used to place a drop of Kit solution onto the MFC coated paper from a height of approximately 13 mm. The drop was left on the paper surface for 15 seconds before wiping away with tissue. If the sample passed this Kit solution, the drop of solution remained on top of the paper. A fail was noted if a dark colour formed under the drop, caused by penetration of the testing solution into the base sheet. The base sheet (both lab made bases and the Suzano paper reel base) failed Kit solution 1 so any grease resistance improvement was assumed a result of the MFC coating. If a sample passed a Kit solution, a higher number Kit solution was tested. If a sample failed a Kit solution, a lower number Kit solution was tested. The Kit number for a sample was the highest passing solution number. The Kit test was repeated until the same result was reached three times on a sample. Any darkening colour of the base sheet, even that which was clearly caused by small pinholes in the MFC coating, was labelled as a fail.

For effective use of the Kit test, it must be apparent whether or not a sample has failed or passed a particular solution. For this reason, the Kit number was only measured on MFC coated paper and base sheets and not on MFC films. This is because MFC films were translucent which made it impossible to reliably distinguish a passing and failing sample.

3.12.4 Oxygen Transmission Rate (OTR)

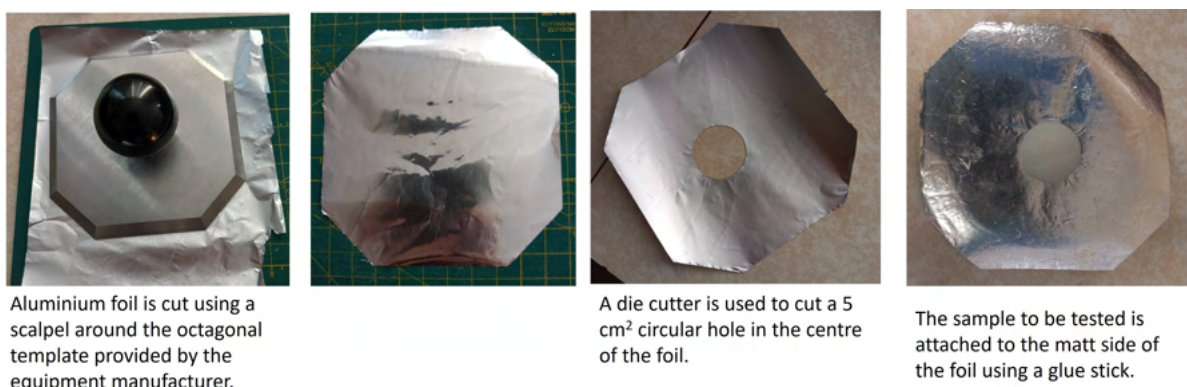
Oxygen transmission rate was measured on MFC films using an Ametek Mocon Ox-tran model 2/22. Oxygen was used as the testing gas. The carrier gas was composed of 5:95 $H_2 : N_2$. Caterwrap aluminium foil was used to produce a mask over the sample in order to reduce the testing area to 5 cm². The foil was cut around the octagonal template provided by the equipment manufacturers using a scalpel. A die cutter was used to place a 5 cm² circular hole in the foil mask. This process is shown in Figure 3.13 The MFC film was also cut using the octagonal template and a scalpel. Following this, a UHU stic glue stick was used to cover the matt side of the foil in a layer of glue. The MFC film was then glued to the foil mask. The analysis of the OTR then assumes that oxygen can only diffuse through the exposed area of the MFC film. In reality, it is likely that the seal between the foil and the MFC film may not be perfect and some additional diffusion of oxygen could occur.

Apiezon- T medium temperature vacuum grease was used to adhere the sample into the testing cell and to grease the testing cell as described in the manufacturers testing manual.¹⁶¹ After this, the testing cell was clamped into the testing chamber. The OTR test was performed at 23°C and a 50% RH environment was used for the carrier and testing gases. The test was run on "Auto" mode and left until a plateau had been reached. This plateau was defined

Table 3.5Composition of Kit Test solutions by volume percent¹⁵⁹

Solution number	Castor oil vol%	Toluene vol%	Heptane vol%
1	100	0	0
2	90	5	5
3	80	10	10
4	70	15	15
5	60	20	20
6	50	25	25
7	40	30	30
8	30	35	35
9	20	40	40
10	10	45	45
11	0	50	50
12	0	45	55
13	0	35	65
14	0	25	75
15	0	15	85
16	0	0	100

as a decrease of less than 2.5% from the previous value. MFC film samples were tested in duplicate but not simultaneously. The "Auto" mode uses a 15 minute examination time. A Re-Zero cycle is performed at the beginning of the test sequence to measure the baseline of the instrument. Following this, a Re-Zero cycle is performed after every two testing cycles.¹⁶¹

**Fig. 3.13.** Cutting aluminium foil mask and attaching sample for use in the OTR test.

During the OTR test, the testing cell is sealed to prevent air contamination. Oxygen gas is pumped into and out of one side of the test cell, exposing the gas to one side of the sample. A catalyst is used to remove hydrogen from the carrier gas and, following this, the carrier gas (now only nitrogen gas) is pumped into and out of the other side of the test cell, exposing the gas to the other side of the sample. Oxygen gas can then diffuse across a concentration gradient through the sample and into the carrier gas. The oxygen concentration of the carrier gas is then measured to determine how much oxygen has passed through the sample.¹⁶¹ The Mocon Ox-tran uses a Coulox oxygen sensor. When oxygen is present in the carrier gas, an electrical current is generated in the sensor and the size of the electrical current is proportional to the oxygen concentration at the sensor.

Occurring at the anode: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ Occurring at the cathode: $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$

The current created at the sensor is measured to calculate the OTR. The instrument performs a calibration to record the transmission rate at sea level barometric pressure.¹⁶¹

During the testing, a graph of OTR vs time is produced by the machine. An example of such a graph for the measurement of an MFC film is shown in Figure 3.14. The pattern of an exponential decrease in measured OTR over time was seen for all MFC films tested. The final OTR was determined as the value at which there was a less than 3% decrease from the previous OTR measurement, which is seen as the difference between the final two points on Figure 3.14. The exponential decrease in measured OTR over time using a Mocon Ox-Tran has been observed in other studies.^{162,163} Possibly this effect is due to residual oxygen within the system, within the cellulose film or in air spaces between the foil mask and the cellulose film. Once this residual oxygen is expelled as the experiment runs, an equilibrium flow rate is reached because the MFC films are good barriers and prevent further oxygen from being transported through the sheet.

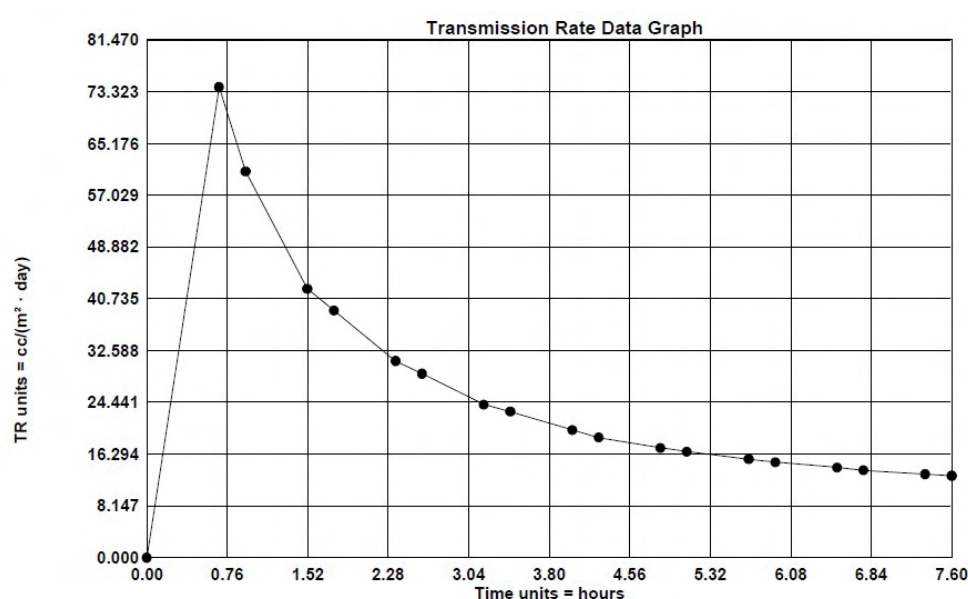


Fig. 3.14. Data output from Mocon Ox-Tran describing change in oxygen transmission rate over time.

Effect of Coating Method and Coating Weight on the Barrier Properties of MFC Coated Paper

4.1 | Introduction

The research project aimed to determine how MFC degree of fibrillation, or degree of separation of fibres into fibrils, affects barrier properties of MFC coatings on paper or cardboard. In order to compare different MFC samples, a suitable laboratory method for coating paper with MFC was required. It is important to understand how much MFC is required for barrier applications so that a suitable coat weight can be selected to compare different samples, however this information is also important to understand for industrial coating applications.

This thesis chapter describes the use of manual laboratory rod coating to apply MFC to a paper base and compares the manual rod coating method with vacuum filtration of a dilute MFC suspension onto a paper substrate. Vacuum filtration was found to produce even, uniform coatings, whereas the manual rod coating method could not evenly distribute MFC across the paper surface. Therefore, vacuum filtration was selected as the main coating method used in this research project.

In addition, this section of the research project aimed to compare a Fiberlean Technologies laboratory method to simulate coating MFC in the wet end of a paper machine with the more time effective method of coating MFC onto a re-wetted paper substrate. This involved laboratory vacuum filtration coating on both a freshly made base sheet and also onto a paper reel cut to fit the vacuum filtration mesh and re-wetted. In order to compare the two methods and to determine a suitable MFC coat weight to use in order to compare different MFC samples later in the research project, the MFC coat weight was increased across both base substrates until optimum barrier properties were reached. MFC coat weight was increased by increasing the concentration of MFC within the dilute suspension used for vacuum filtration.

4.2 | MFC used in the Coating Process

An MFC made from Northern Bleached Softwood Kraft (NBSK) (Northern Bleached Softwood Kraft) pulp which was produced at Fiberlean Technologies Ltd in their production plant in Cornwall was used in the coating process. Optical microscope images taken of an 0.08% MFC suspension using a Differential Interference Contrast microscope are shown in Figure 4.1.

This MFC sample was also used laboratory manual wire rod coatings. The MFC sample was received at a solids content of 0.73%. In order to increase the solids content to allow application of a higher MFC coat weight to the sheet surface, the MFC suspension was thickened through centrifugation in a Rotana centrifuge until a clear boundary between MFC gel and water was formed. Water was then removed from the top of the container using a plastic pipette. The final solids content used for the laboratory rod coatings and the vacuum filtration coatings

used as comparison points to the laboratory rod coatings was 1.1%. For the laboratory rod coating process, the MFC was applied at a 24 μm wet film thickness. A sheet coated in the same methods but with water only was also included as a control.

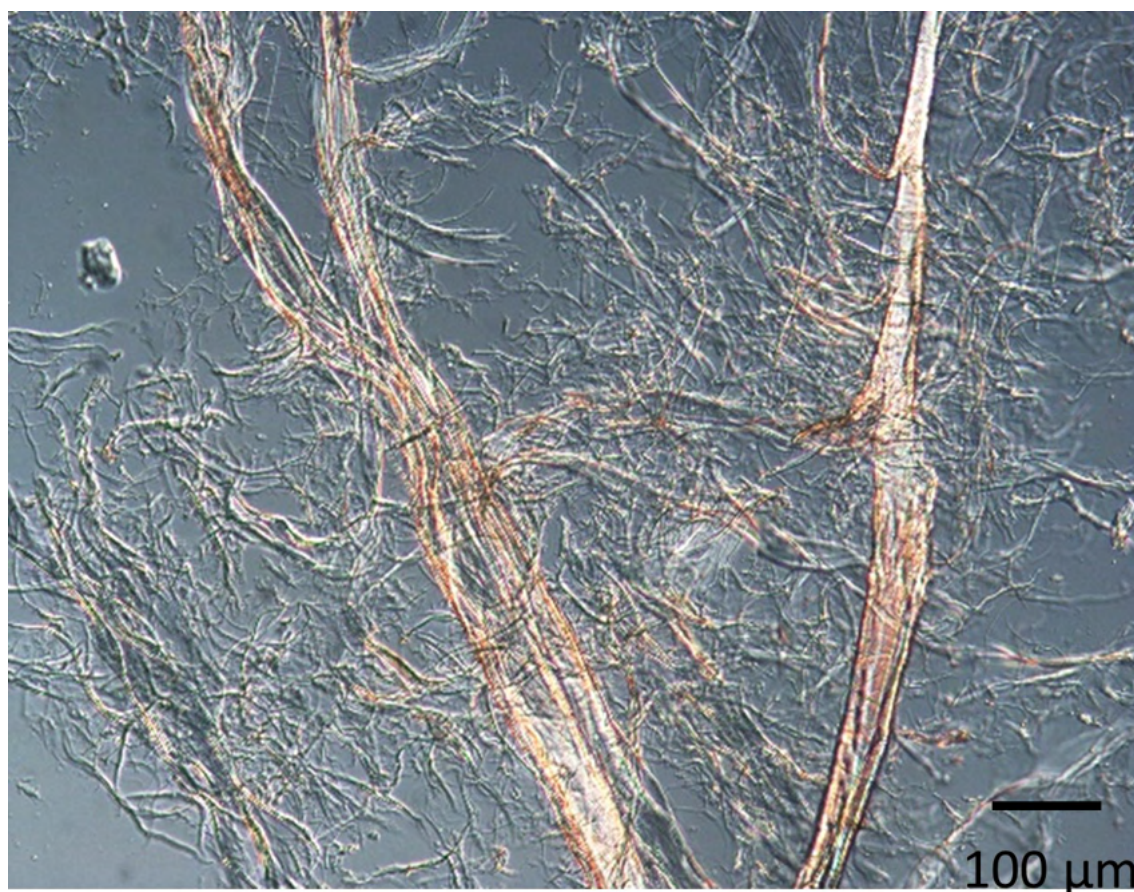


Fig. 4.1. DIC optical microscope image of 0.08 wt% aqueous MFC suspension used for coating onto base papers.

Selected Valmet fibre image analyser properties relating to the fines content, extent of fibrillation and length weighted length distribution of the MFC sample are shown in Table 4.1.

Table 4.1

Valmet fibre analyser properties of MFC used in coating process. For definitions of fibre image analyser parameters please see Table 4.1

Lc(l) [mm]	Fines A [%]	Fines B [%]	Fibrillation [%]
0.324	61.5	31.48	6.17

4.3 | Results and discussion

4.3.1 Comparison of MFC Coating via Laboratory Rod Coating or Vacuum Filtration

The feasibility of coating MFC through manual rod coating in the laboratory was addressed with a short study. The same MFC sample and base paper were used in both rod coating and coating through vacuum filtration. Figure 4.2 shows a comparison of rod coating with coating MFC via vacuum filtration. The coat weight of MFC applied through vacuum filtration was assumed to be the same as the mass of MFC used in the coating process. In the case of rod coating, the MFC coat weight was calculated by subtracting the grammage of the sheets coated with water only from those coated with MFC. It is apparent that a significantly lower Bendtsen porosity was reached for MFC coated through vacuum filtration. The different values of Bendtsen porosity of the base sheet refer to controls for the different coating processes. The "base sheet" value is the base sheet with no alterations, the zero coat weight sample for vacuum filtration refers to a sheet with water only filtered through, and the zero coat weight sample for the laboratory rod coating samples refer to a rod coating with water only.

During the rod coating process, it was clear that the MFC was not being applied in a uniform film. Large bundles of MFC were forming on the paper surface during the draw down process and the effect was lumps of MFC rather than a smooth continuous film of MFC. This could have explained the large difference in Bendtsen porosity between the rod coating and vacuum filtration coating processes.

Mazhari Mousavi and co-authors also reported difficulty in coating MFC suspensions evenly using a laboratory wire round rod coating procedure, explaining that lumps of fibrils formed during the coating process which is the same effect observed in this research project.¹¹⁹ Several studies have found that when coating MFC onto a dry base paper using the application of a rod or blade coating system, carboxymethyl cellulose is required in the coating suspension to reduce suspension viscosity and reduce dewatering of the coating suspension into the base sheet. This prevents water being rapidly drawn into the base sheet and increasing the viscosity of the MFC suspension, and therefore helps with the application of a more uniform coating layer.^{118,119,164}

Figure 4.3 shows SEM images of the base sheet, the MFC coated using the rod coating process at approximately 1.29 g m^{-2} and MFC coated using vacuum filtration at 1 g m^{-2} . It was apparent that a better and more uniform coverage was achieved by coating MFC through vacuum filtration rather than manual laboratory rod coating.

The focus of this research project was to understand the effect of cellulose degree of fibrillation on barrier properties of MFC coatings. In order to achieve this, a method of coating MFC which produced a smooth, uniform MFC layer was required so that different MFC samples could be compared fairly. For this reason, vacuum filtration was selected as the laboratory based MFC coating method used in this research project. Although the research topic of altering the rheological properties and dewatering rate of MFC suspensions to improve coating uniformity is an interesting topic of research, it is beyond the scope of the current work which is focused on how MFC properties affect barrier properties of MFC coatings.

4.3.2 Surface structure of MFC coated sheets

MFC coating through vacuum filtration was performed using two different methods. The first was developed by Fiberlean Technologies as a method to apply MFC through vacuum filtration onto a freshly formed base sheet.¹²¹ This laboratory method aimed to simulate the industrial wet end coating process. As a comparison, MFC was also coated via vacuum filtration onto a

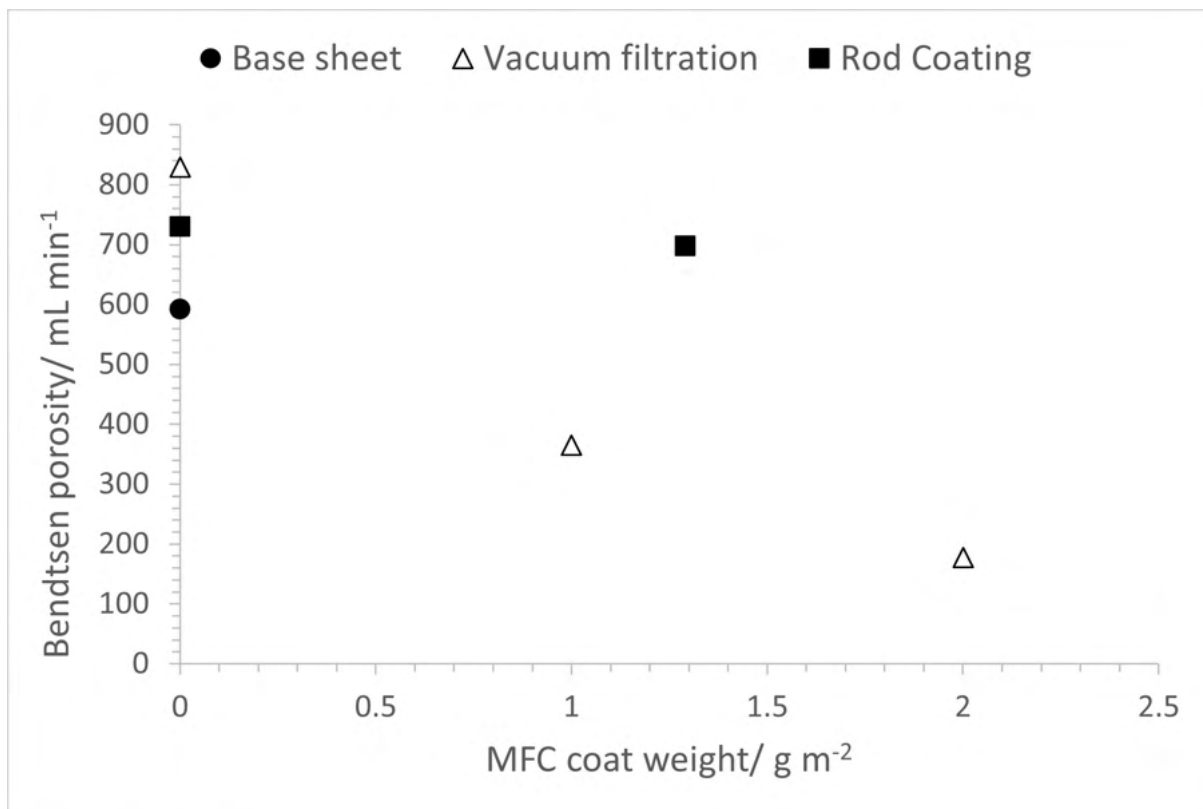


Fig. 4.2. Comparison of the effects of coating MFC through either vacuum filtration or manual rod coating on paper Bendtsen porosity.

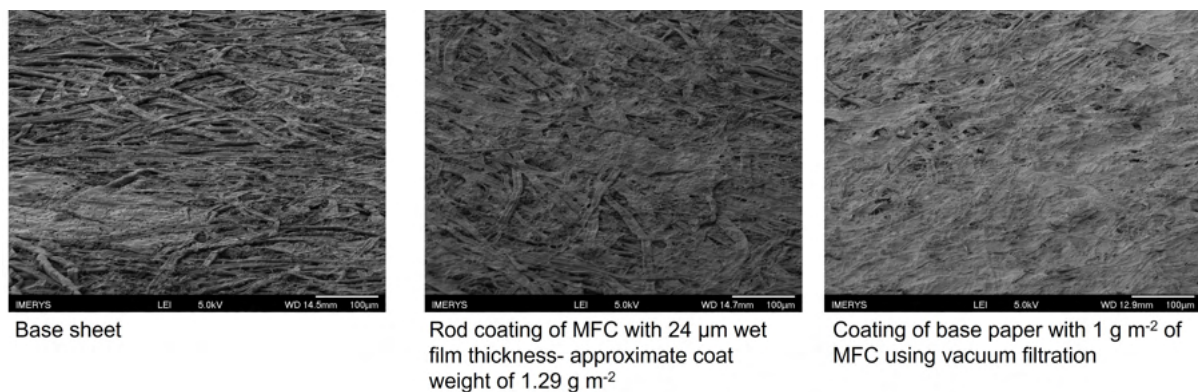


Fig. 4.3. SEM images of the base sheet used in coating, base sheet coated with MFC via the rod coating process and base sheet coated with MFC via vacuum filtration

re-wetted paper reel base. For more information on the coating methods, the reader is referred to the Experimental chapter of the thesis.

Figure 4.4 shows how the surface structure of a lab made base sheet changes upon coating with MFC using vacuum filtration followed by hot pressing. The base sheet has an open structure, showing a large amount of porosity between fibres. As the MFC coat weight increases, the porous structure of the base sheet becomes covered in an MFC layer with significantly lower surface porosity. When 8 g m⁻² of MFC is coated on the paper surface, there is an almost continuous film of MFC covering the fibrous base.

Figure 4.5 shows height profile images of the freshly lab made base sheets coated with increasing coat weights of MFC. These images clearly show the fibrous structure of the base sheet and the

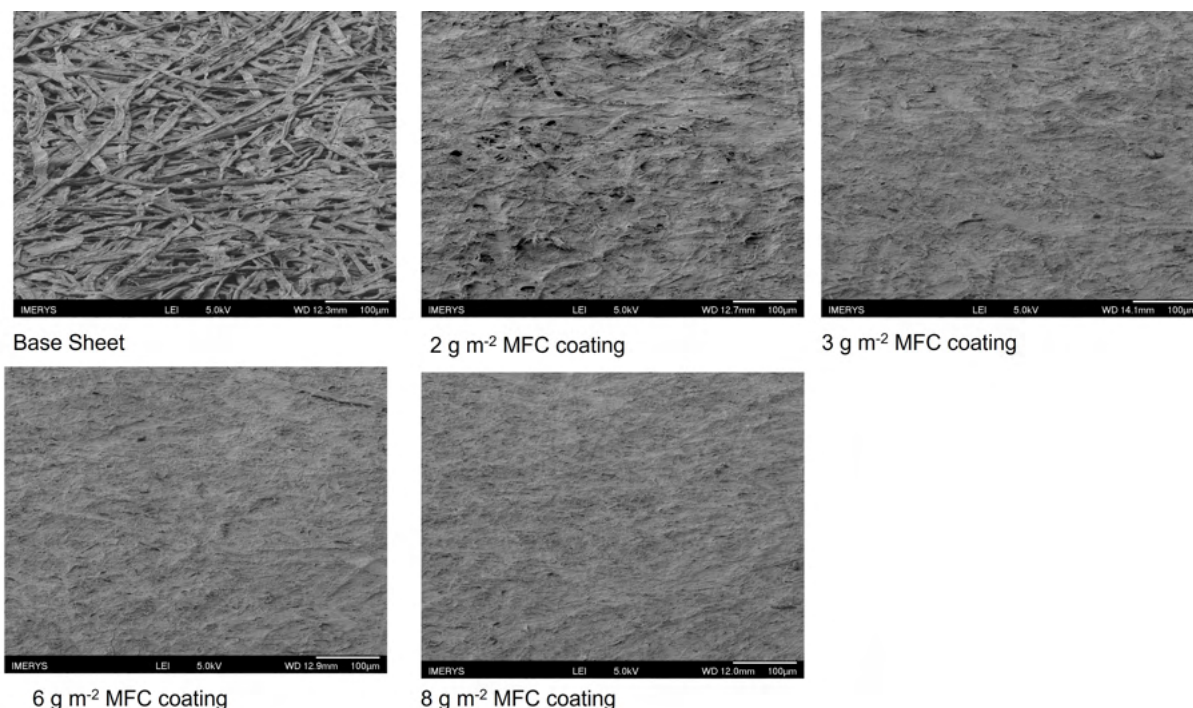


Fig. 4.4. Tilted SEM images of lab made base sheet and lab made base sheets with increasing coat weight of MFC

reduction in height variation seen as the MFC coat weight increases and a smoother surface appears. From the height profile images, it can be seen that when 2 g m^{-2} of MFC is applied, the rough base sheet is mostly covered with a layer of MFC. When comparing to the SEM images of the same samples shown in Figure 4.4, it can be seen that while an MFC film has been applied, it is not continuous. This is not visible in the laser height profile images, possibly because the resolution is $2 \mu\text{m}$ and the defects in the MFC layer may be smaller than this. Nevertheless, the image from laser profilometry allows the visualisation of the paper coated surface. This is significant because the laser profilometer is more readily accessible and many samples can be imaged.

Figure 4.6 shows interferometric laser profilometry height profile measurements of the paper reel base sheet and sheets coated with increasing MFC coat weight. Similarly to Figure 4.5, the base sheet has a visibly rougher surface which is covered by a smooth MFC film at a coat weight of approximately 4 g m^{-2} . The laser height profile images show a less clear contrast between the base and MFC coated sheets for the sheets coated on the paper reel base. This could be because this base had a smoother surface before being coated with MFC. For example, the lab made base sheets had a PPS roughness of $6.47 \pm 0.03 \mu\text{m}$ whereas the paper reel base sheets vacuum filtered with just water and dried in the Rapid Köthen driers had a PPS roughness of $4.74 \pm 0.02 \mu\text{m}$, both measured at 1000 kPa. Therefore, there may have been more height variation in the lab made base sheet which made the contrast of coating the rougher base sheet more clear in the laser profilometry height images.

4.3.3 Effect of MFC coating on Bendtsen porosity of sheets

Figure 4.7 shows how increasing MFC coat weight decreased Bendtsen porosity for both base sheets. Since Bendtsen porosity is a measure of air permeability, increasing coat weight of MFC decreased air permeability of the sheet.

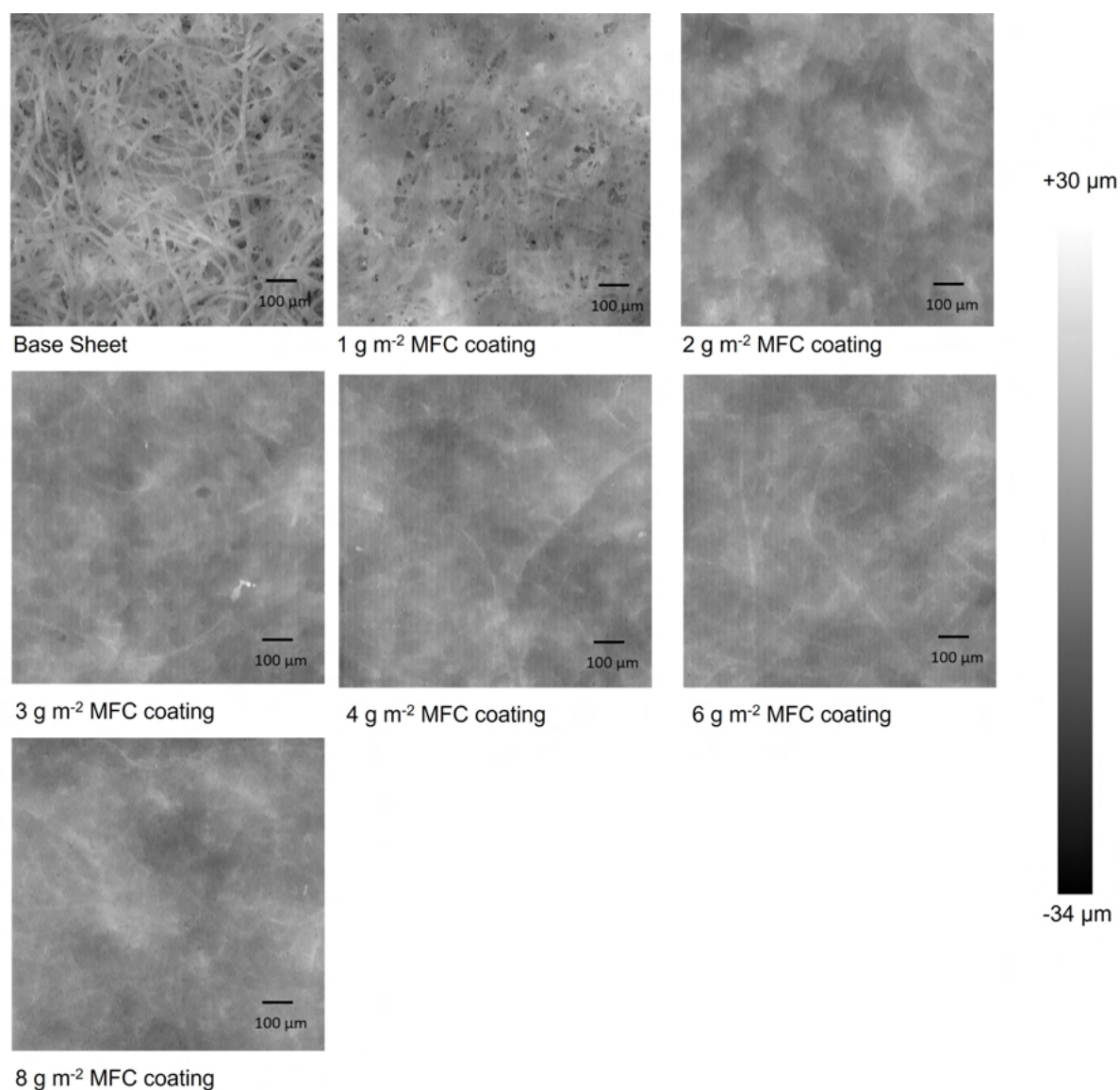


Fig. 4.5. Height profile images of MFC coated lab made base sheets recorded using an interferometric laser profilometer.

Coating porous board substrates with MFC has been shown to significantly decrease air permeability of the sheet due to the dense MFC layer preventing air flow through pores in the base.^{26,28,31,67} Kumar and co authors found that 5 g m^{-2} of a blend of 95% MFC and 5% carboxymethyl cellulose coated onto a base paper board using a roll to roll process reduced the Bendtsen porosity of the base paper from 385 mL min^{-1} to the lower detection limit of the instrument.¹⁶⁵ In Figure 4.7, 8 g m^{-2} of MFC is required to reach the detection limit of the Bendtsen porosity instrument for both bases. The difference in the coat weight of MFC required to reach the lower detection limit of the instrument could be because the study of Kumar and co-authors used different instruments to measure air permeability than were used in the current study, the Carboxymethyl cellulose added into the suspension may have helped to seal surface pores in the coating, and the surface and pore structure of the base paper were likely to be different.

From the Bendtsen porosity data, it appears that a lower coat weight of MFC is required to reach a minimum Bendtsen porosity value for the MFC coated onto the freshly formed base sheets compared to the sheets where MFC is coated onto the commercial paper reel base.

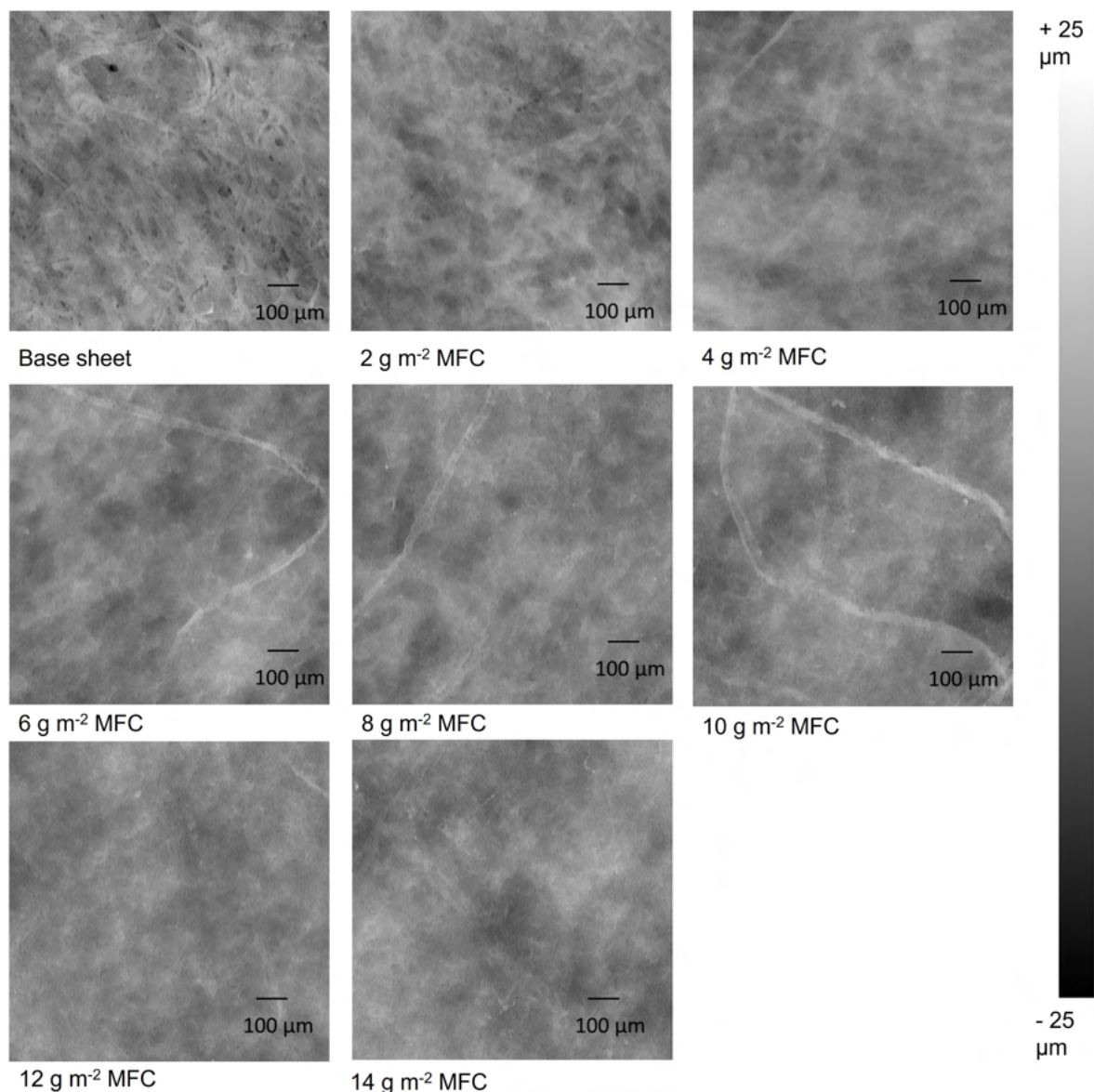


Fig. 4.6. Height profile images of MFC coated paper reel base recorded using an interferometric laser profilometer.

The difference may have been because the freshly made base sheet had not yet been pressed when the sheets were made and therefore the two layers may have been pressed together more effectively in the driers, leading to fewer defects in the MFC coating.

4.3.4 Effect of MFC coating on heptane vapour barrier properties of sheets

Figure 4.8 shows that for both base substrates, an MFC coat weight of at least 4 g m^{-2} is required to decrease HVTR from the value of the base sheet. Figure 4.4 shows that at an MFC coating of 3 g m^{-2} , the fibrous structure of the base is still visible under the MFC coating and there are many small pores in the MFC web. It could be that this structure is not compact enough to provide a significant barrier to heptane vapour.

The HVTR of the lab made base sheet was $2227 \pm 13 \text{ g m}^{-2} \text{ day}^{-1}$ and the paper reel base was $2353 \pm 59 \text{ g m}^{-2} \text{ day}^{-1}$. This may be the upper limit of values that the HVTR test can measure. Hu and co-authors proposed that when WVTR is measured filling a permeation cup

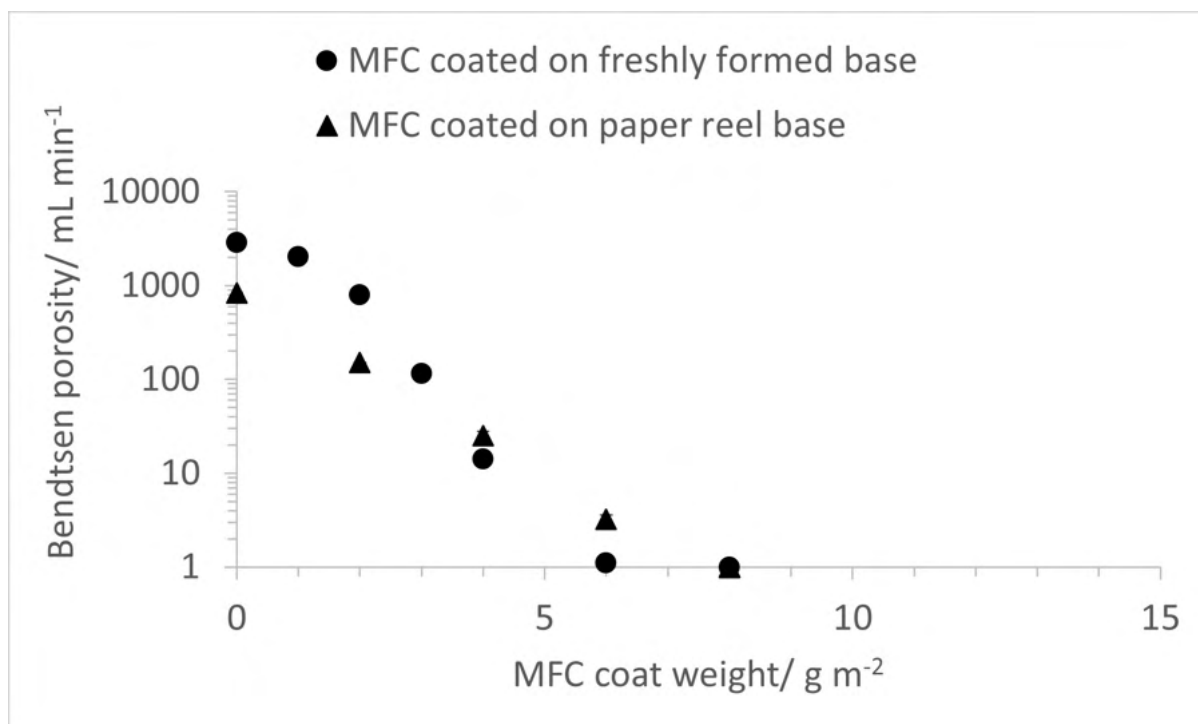


Fig. 4.7. Graph showing the effect of increasing MFC coat weight on two base paper substrates on the Bendtsen porosity of the MFC coated paper. Bendtsen porosity is shown on a logarithmic scale. Each data point came from a minimum of 5 measurements. Error bars show standard errors of these 5 measurements.

with water and measuring mass lost over time, WVTR may be underestimated for highly water permeable materials. The authors explained this as due to the rate of evaporation and diffusion of water inside the cup was lower than the rate of diffusion through the testing material, therefore reducing RH inside the cup.¹⁵⁷ It is likely that the same situation is occurring in Figure 4.8, where the HVTR test requires a threshold of resistance to heptane vapour transport before the property can be accurately measured since the rate of HVTR through uncoated paper may be greater than or equal to the rate of evaporation of heptane.

When testing MFC coated papers, it became clear that there may also be a lower limit of reliability to the HVTR test. It was observed throughout the experimental work undertaken in this research project that when the HVTR values of coated papers decreased to a limit of approximately $30 \text{ g m}^{-2} \text{ day}^{-1}$, brown staining could be observed around the outside of the papers. When the cups were disassembled after the experiments, it was apparent that heptane vapour had condensed onto the side of the paper which was inside the cup, leaving a brown ring where the heptane had condensed between the rubber gasket and the paper. This effect can be seen after the measurement of HVTR of MFC films in Figure 4.9. This could reduce reliability of the results as the liquid condensed heptane may damage the MFC layer after prolonged contact during the test, therefore allowing faster heptane vapour diffusion. It also could mean that heptane is being transported through the edges of the MFC coating through capillary action as a liquid and then evaporating, therefore possibly leading to a higher HVTR than would be observed through gas diffusion alone.

For both bases, 8 g m^{-2} was required to reach a HVTR of below $30 \text{ g m}^{-2} \text{ day}^{-1}$. Kumar and co-authors measured a HVTR of 0 at an MFC a coat weight of 95% MFC and 5% carboxymethyl cellulose of 6 g m^{-2} .¹⁶⁵ This is lower than the MFC coat weight required to reach a HVTR below $30 \text{ g m}^{-2} \text{ day}^{-1}$ for both base substrates shown in Figure 4.8. The

difference could be because the base used by Kumar and co-authors had a Bendtsen porosity of 385 mL min^{-1} which is lower than either of the bases used in this research project ($2891 \pm 21 \text{ mL min}^{-1}$ and $829 \pm 27 \text{ mL min}^{-1}$), and therefore less MFC may have been required to form a dense film on the surface as more was retained on the sheet surface. It is also possible that differences in the chemical compositions of the base sheet, for example the pulp types used and any drainage aids or sizing agents, may have affected how the MFC layer formed on the base sheet.

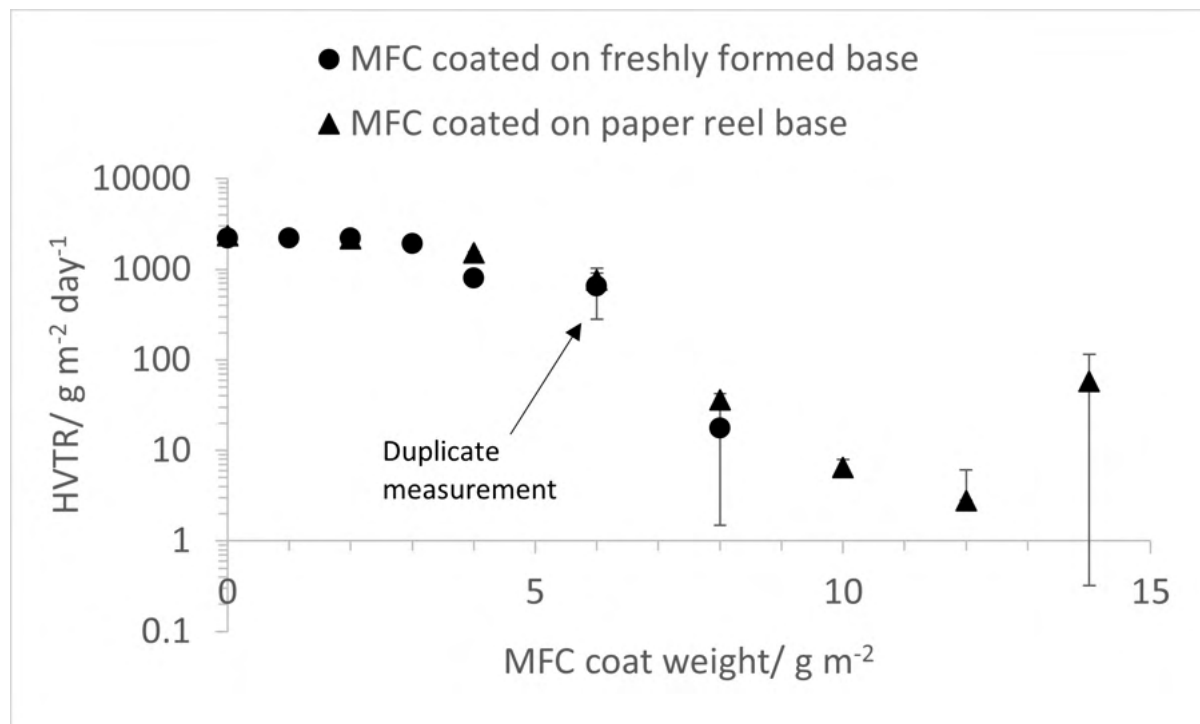


Fig. 4.8. Graph showing the effect of increasing MFC coat weight on two base paper substrates on the HVTR of the MFC coated paper. HVTR is shown on a logarithmic scale. Each data point came from triplicate measurements unless otherwise stated. Error bars show standard errors of these 3 measurements.

4.3.5 Effect of MFC coating on grease resistance of sheets

Figure 4.10 shows how increasing MFC coat weight on either a freshly made lab base sheet or a paper reel base affected grease resistance, measured through the Kit test. A Kit number of 1 meant in this case that either the lowest Kit solution number (pure castor oil) penetrated through the sheet or that the second Kit solution failed. An increasing Kit number corresponds to the coated sheet retaining a higher number Kit solution on the surface without penetrating through to the base. A kit number of 16 corresponds to the highest measurable Kit number—this means that a drop of n-heptane did not penetrate through the sheet after 15 seconds. Increasing MFC coat weight increased grease resistance of the sheets for both bases. The improvement was more rapid for MFC coated on a freshly formed base than for the MFC coated onto the paper reel base and a lower MFC coat weight was required to reach the maximum Kit value. This effect appeared to be due to pinholes in the MFC coatings on the paper reel base allowing transport of the Kit solutions. It was unclear why pinholes were more prominent in MFC coatings on the commercial re-wetted base in comparison to the freshly formed base sheets. This may be related to differences in chemical composition between the

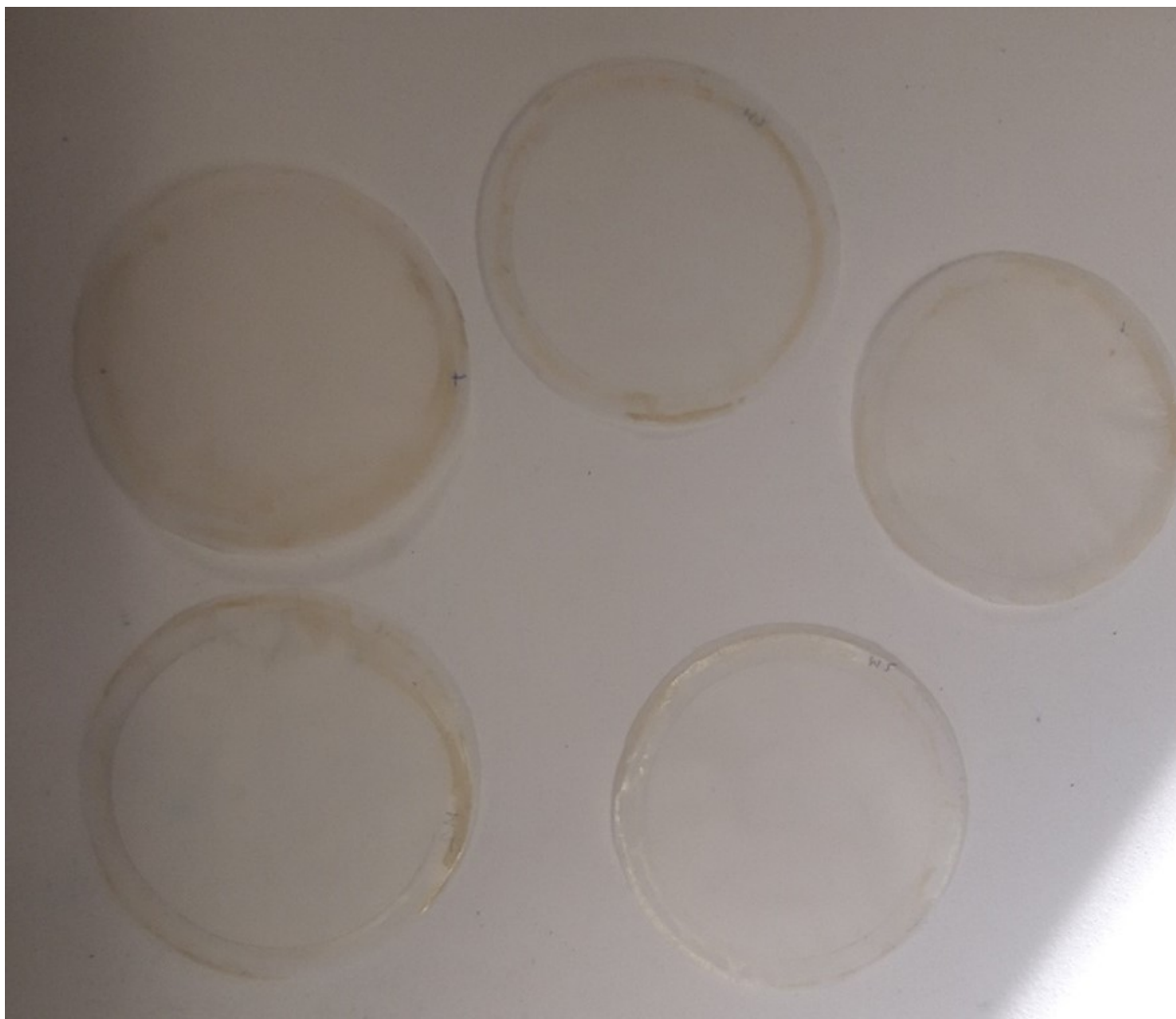


Fig. 4.9. Photograph showing discolouration on MFC films after a HVTR measurement

two base sheets, or possibly could be related to differences in adhesion between the MFC and the base sheet using the two different methods.

Yook and co-authors found that increasing MFC coat weight on a woodfree base paper increased Kit number and that a maximum Kit number (12) was reached at an MFC coat weight of 8 g m^{-2} for an MFC sample produced through grinding using a Supramasscolloider.³¹ 8 g m^{-2} is the same coat weight required in this study to increase Kit number to 16 for the freshly formed base sheets. For the paper reel base, a higher MFC coat weight of 14 g m^{-2} was required. Kumar and co-authors also found that increasing MFC coat weight increased the Kit number of MFC coated paper, with a Kit number of 10 reached at an MFC coat weight of 11 g m^{-2} .¹⁶⁵ It is difficult to directly compare results from different studies due to the use of different base substrates, coating methods and MFC production methods but it can be seen that increasing MFC coat weight is beneficial to improving grease resistance.

4.3.6 Method Selection for Applying MFC through Vacuum Filtration

The purpose of this part of the study was to answer several questions about the best method to coat MFC in order to compare the barrier properties of MFC samples with different degrees of fibrillation. The following topics were addressed.

1. What type of base paper should be used for coating MFC with vacuum filtration?

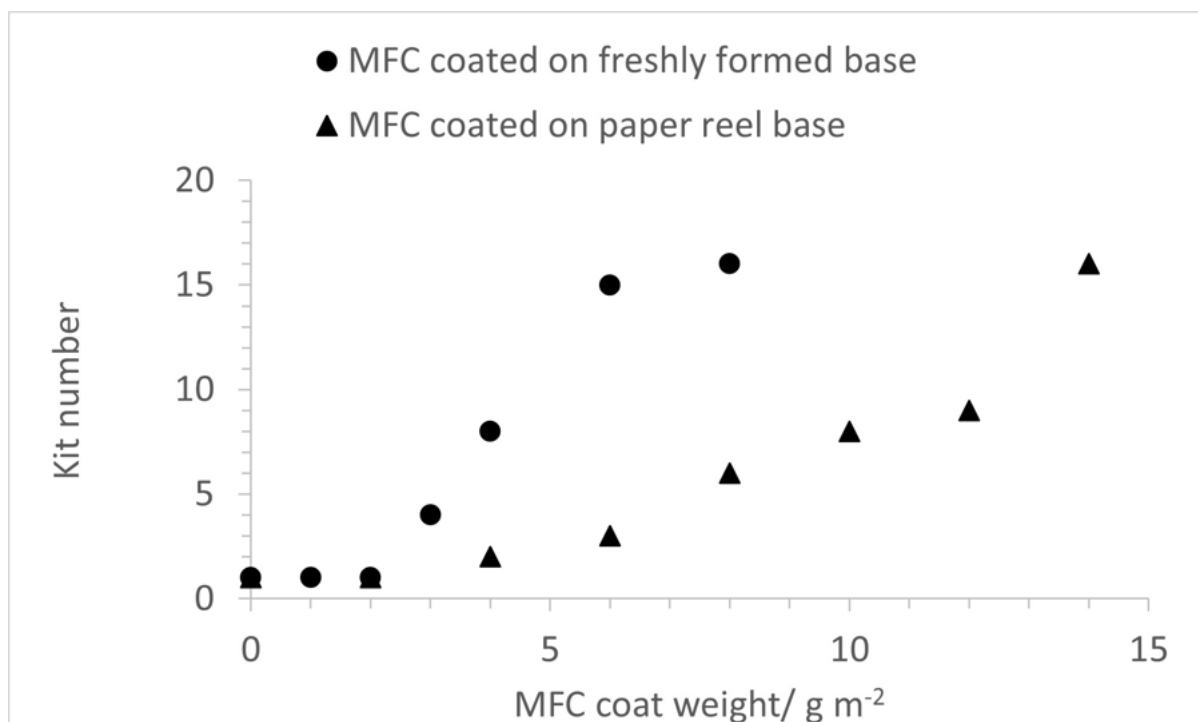


Fig. 4.10. Graph showing the effect of increasing MFC coat weight on both a freshly made lab sheet and a paper reel on the grease resistance of the coated paper- increasing grease resistance is measured as a higher Kit number.

2. What MFC coat weight should be used to compare different MFC samples?

Figures 4.7, 4.10 and 4.8 show that increasing MFC coat weight decreased air permeability and HVTR and increased grease resistance for both base sheets. An advantage of using a freshly made lab base is that it more closely resembles the Fiberlean Technologies industrial process of coating MFC onto a wet paper base which we are trying to replicate in the lab. In addition, making the base paper allows precise control of the composition: for example, the addition of mineral, sizing agents or surface treatments can be avoided. Since the research project took place over a period of four years and involved the making of an extensive number of MFC coated sheets, multiple batches of pulp would have had to have been made up over the course of the project. Therefore, using a paper reel base allows for a more consistent coating substrate without variation between batches of pulp. In addition, the use of the paper reel base saves experimental time since making both the batches of pulp and the base sheets can be avoided. The issue of the presence of mineral and potential use of sizing agents or other surface treatments in the paper reel base is mitigated by using the same reel and always coating on the same side of the paper so that the coating surface was consistent. For these reasons, the paper reel base was selected as an MFC coating substrate for further work in the project.

10 g m^{-2} was chosen as the MFC coat weight for comparing NBSK pulp samples with increasing degrees of fibrillation in the next chapter. This was because the NBSK MFC sample used in the present thesis chapter, when coated at 10 g m^{-2} , allowed room for improvement in the grease resistance test if other MFC samples formed better barrier layers and would have shown any decrease in barrier properties through increases in HVTR and Bendtsen porosity.

4.4 | Conclusions

The purpose of the research described in the current thesis chapter was to determine the most effective laboratory method for coating paper substrates with MFC in order to effectively compare how MFC degree of fibrillation affects barrier properties in later work. It was shown that manual laboratory rod coating did not produce even MFC coatings, possibly due to the high viscosity and rapid dewatering of MFC suspensions. Through coating MFC using vacuum filtration, it was apparent from SEM images of sheet surfaces that increasing MFC coat weight allowed an application of a uniform film of MFC on the paper surface. This resulted in decreased air permeability and HVTR and increased grease resistance as MFC coat weight increased. The paper reel base was selected as the coating substrate for the remainder of the research project and an MFC coat weight of 10 g m^{-2} was selected as the coat weight to compare different MFC samples in the following research.

Influence of Degree of Fibrillation of Cellulose Fibres on Barrier Properties of MFC

5.1 | Introduction

The main purpose of the research project was to understand the extent of separation of cellulose fibres into nanofibrils required to produce optimal barrier properties when coated industrially at the wet end of a paper making process. An additional aim of the research project was to find a quantitative measure of MFC properties that could be used to select samples that may be effective barrier layers. This is because barrier testing is time consuming and requires special training and the use of hazardous solvents. Finding another method to screen MFC samples would reduce the need for extensive barrier testing of a wide range of samples.

The present chapter investigates how increasing the extent of mechanical treatment on NBSK (Northern Bleached Softwood Kraft) pulp affected the degree of fibrillation of the MFC. This was determined through optical microscope imaging and fibre image analyser measurements. The MFC samples with increasing degree of fibrillation were then coated as 10 g m^{-2} layers onto the Suzano commercial base paper through vacuum filtration as described in Chapter 4 so that air permeability, HVTR and grease resistance could be measured. In addition, 50 g m^{-2} sheets of MFC or refined pulp were also made using vacuum filtration and tested for WVTR.

Cellulose was produced from the same bleached kraft pulp source (NBSK) at increasing levels of fibrillation as described below:

- Pulp refined in a laboratory Valley Beater
- MFC produced using the Fiberlean Technologies process by grinding in a wet stirred media mill with increasing energy
- MFC produced using the Fiberlean Technologies grinding process with an additional homogenisation stage to create more finely dispersed cellulose. The homogenisation pressure was varied to further increase cellulose dispersion.

Increasing degree of fibrillation of cellulose is thought to improve the barrier properties of MFC films, up to the point where a film with no connecting porosity is formed. However, increasing degree of fibrillation through increased mechanical processing can lead to decreased crystallinity index of the cellulose. Decreasing crystallinity of cellulose may result in a less effective barrier layer.^{1,26,58,83,85,93,105} Therefore, in present thesis chapter the effect of increasing mechanical treatment on cellulose crystallinity was measured through use of XRD and FTIR on cellulose films. The WVTR of the cellulose films was also measured to determine if increasing degree of fibrillation of cellulose is more influential than crystallinity on the WVTR of cellulose films. Belbekhouche and co-authors found that films of CNC showed a higher water vapour and

oxygen diffusion coefficient than films of MFC, suggesting that the entangled structure of MFC may be more important than crystallinity in determining barrier properties.⁷³ The present study aimed to determine if changing the film structure by increasing fibrillation, leading to a lower degree of connecting porosity, would be more influential to the water vapour barrier properties than any resulting decrease in crystallinity index as a result of increased mechanical treatment.

5.2 | Experimental

5.2.1 MFC Sample Details

MFC was made by Fiberlean Technologies at the production plant in Cornwall from Botnia RMA90 bleached kraft pulp. Samples were produced by grinding in a wet stirred media mill at increasing energy from 3000 to 6000 k W h t⁻¹. A batch of MFC was produced at 4000 k W h t⁻¹ which was then homogenised at increasing pressures from 200 to 1000 bar. The MFC samples were dosed with biocide to prevent spoilage during storage.

5.2.2 Refined pulp sample details

Before the research project commenced, a Fiberlean Technologies employee made up samples of refined pulp to be used in the project. Bleached kraft pulp (Botnia RMA90 pine), was refined in a laboratory Valley Beater for increasing lengths of time to produce pulp samples ranging from unrefined pulp at 700 CSF to highly refined pulp at 65 CSF. Pulp from 700 CSF to 390 CSF was de-watered and stored in the fridge as pads which were soaked in filtered tap water for 24 hours and disintegrated using a Messmer benchtop disintegrator for 10 minutes at a pulp solids content of approximately 0.7%. Two cycles of disintegration were performed to ensure that the pulp was properly dispersed. Pulp from 230- 65 CSF could not be de-watered into pads when the pulp was refined due to slow drainage so was stored as a pulp suspension. This was mixed with water and disintegrated twice using the benchtop disintegrator. Canadian Standard Freeness was re-measured once the pulp samples had been made into slurries. The mid point of two measurements was taken as the re-measured CSF value. Once made into slurries, refined pulp samples were sent to Fiberlean Technologies Quality Control department for measurement of FLT index.

5.2.3 MFC coated sheets

MFC was coated onto sheets cut from a Suzano commercial paper reel using vacuum filtration as described in Chapter 4. 10 g m⁻² of MFC was applied to the base paper. Refined pulp samples were also coated in the same way as a comparison point for MFC. The following properties were tested on the cellulose coated sheets:

- Bendtsen porosity
- HVTR
- Kit test

WVTR was not measured on cellulose coated paper since the base paper was highly permeable to water vapour and it was likely that the thin cellulose coatings would not provide enough of a water vapour barrier to get an accurate result from the WVTR test due to issues with the stagnant air layer and silica gel saturation described in Chapter 3. At the time of the study, there was no available equipment for measurement of OTR.

Original provided CSF/ mL	Re-measured CSF/ mL
700	694
550	552
390	439
230	221
130	135
65	66

Table 5.1

Provided and re-measured CSF of refined pulp samples

5.2.4 Refined pulp sheets and MFC films

Ideally, all refined pulp and MFC films would have been made using the same method to allow comparisons in the sheet properties. However, the vacuum filtration device used to make MFC films was not suitable for making sheets from refined pulp as it led to poor sheet uniformity and non uniform sheet weights. Therefore, sheets from refined pulp samples were made in the Messmer British handsheet former since the larger chamber allows dilution of the pulp to much lower solids content before drainage, therefore improving uniformity of the final sheet. It was not practical to make MFC films in this way because the large amount of water would have led to very slow drainage and the nylon filtration mesh could not be applied over the wire mesh. To obtain a uniform sheet weight, all pulp samples were diluted to a consistency of 0.5% and the volume of pulp needed per sheet was measured in a measuring cylinder. As a comparison point, sheets from the 65 CSF pulp were made using both methods. All sheets were dried in the Rapid Kothén hand sheet driers for 7 minutes. The following properties were tested on the cellulose sheets:

- Density through measurement of thickness using digital micrometer and mass per area.
- Crystallinity index through XRD measurement and ATR-FTIR analysis.
- Light scattering properties through diffuse reflectance measurements.
- WVTR

HVTR and Kit test were not measured on the cellulose sheets because it would not have been possible to determine Kit number on the translucent MFC films without the backing of the base paper and the MFC films would have had a HVTR that was too low to be measured due to suspected condensation and wicking of heptane described in Chapter 4.

5.3 | Results and Discussion

5.3.1 Characterisation of cellulose

Re-measurement of CSF

CSF was re-measured for the refined pulp samples after making into a pulp slurry. A comparison between provided and re-measured CSF is shown in Table 5.1. Small differences were seen between the original and re-measured CSF values.

Optical Microscopy of MFC and Pulp Samples

Figure 5.1 shows how the morphology of cellulose fibres changed as the level of refining increases. There was an increase in the level of external fibrillation of fibres as the CSF

increased. This is consistent with what should be expected during the pulp refining process.¹¹⁵ There was little evidence of liberated fines in the refined pulp samples, but they could have been entangled with the larger fibres or may have been too small to be visualised using optical microscopy. Figure 5.2 shows the effect of increasing grinding energy on the morphology of

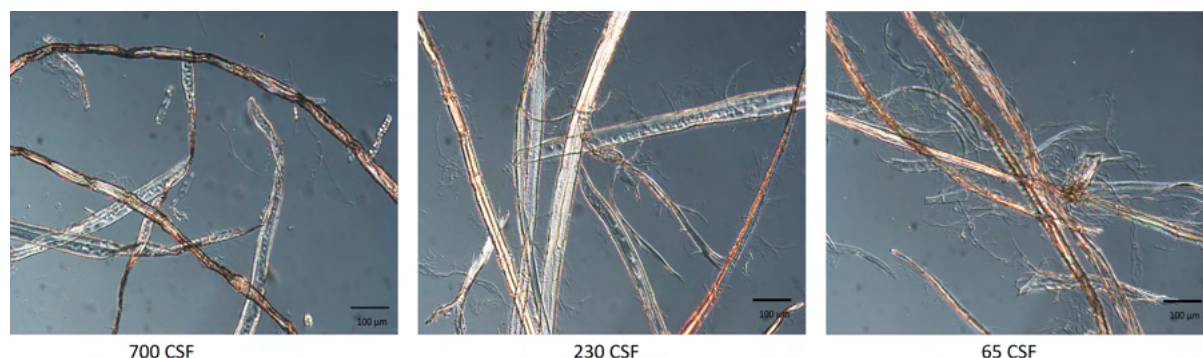


Fig. 5.1. DIC optical microscope pictures of 0.08 wt% refined pulp suspensions.

cellulose samples used in this study. The sample with the lowest grinding energy showed significantly higher fibre fibrillation than the highest level of refined pulp. Increasing grinding energy at first increased fibrillation of fibres, resulting in large, connected aggregates of fibrils. Further increasing grinding energy led to more liberated fibrils but with decreased lengths, indicating that grinding at high energy can cause cutting of the fibrils.

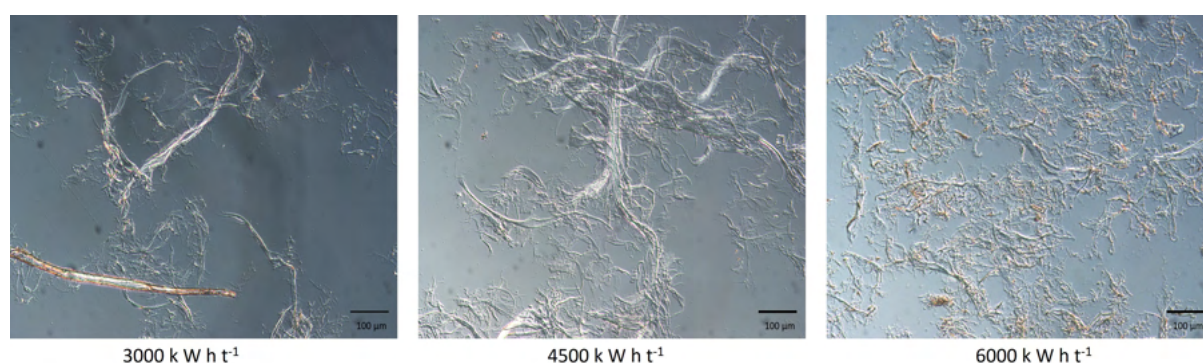


Fig. 5.2. DIC optical microscope pictures of 0.08 wt% suspensions of MFC produced through grinding with increasing energy.

Figure 5.3 shows the effect of increasing homogenisation pressure on the morphology of MFC. The lowest homogenisation pressure created an MFC that was significantly more finely dispersed than the $4500 \text{ k W h t}^{-1}$ MFC sample. The homogenisation feed was ground at $4000 \text{ k W h t}^{-1}$. Furthermore, the fibrils appeared to be longer than the $6000 \text{ k W h t}^{-1}$ MFC sample. As the homogenisation pressure increased, there appeared to be an overall decrease in width of the fibrils. The homogenisation process appears to have helped to disperse aggregates of fibrils into smaller aggregates or liberated fibrils.

Fibre Image Analyser Properties

Figure 5.4 shows the percentage of the length weighted distribution of fibre fragments with a width greater than $10 \mu\text{m}$ in increasing fractions from 0 - 7.6 mm in length for refined pulp samples. The percentage of fibres between 1.2- 3.2 mm decreased as the level of refining increased. In contrast, the percentage of length weighted distribution between 0 - 0.6 mm

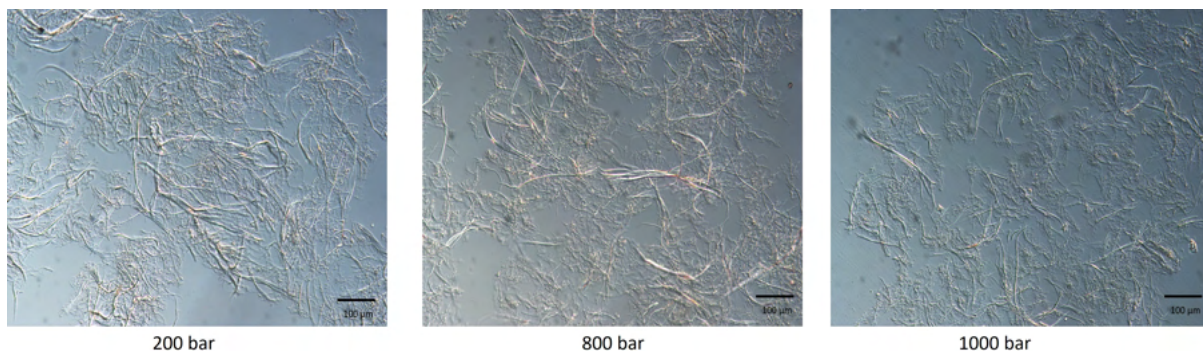


Fig. 5.3. DIC optical microscope pictures of 0.08 wt% suspensions of MFC produced through homogenising with increasing pressure.

increased as refining level increased, indicating the refining process had some cutting effect on the larger fibres.

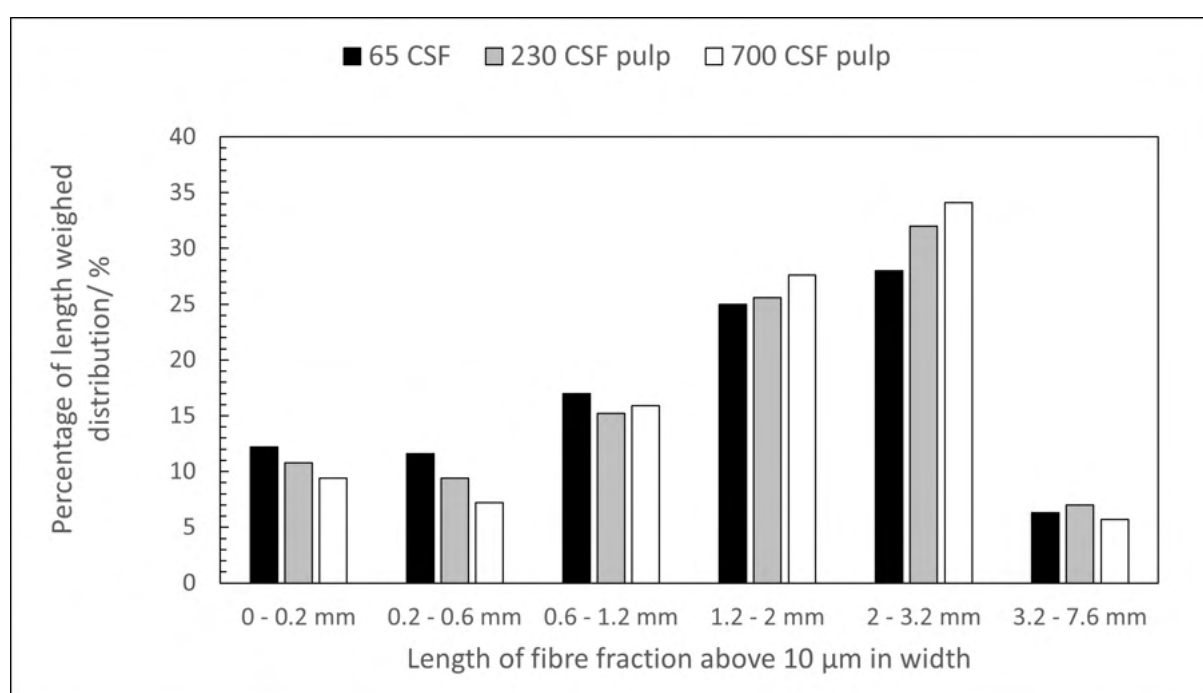


Fig. 5.4. Percentage of length weighted distribution of refined pulp fibres above 10 µm in width in length fractions ranging from 0 - 7.6 mm

Figure 5.5 shows the same information for MFC made using increasing grinding energy. Increasing grinding energy decreases the percentage of length weighted distribution of fibre fragments between 0.6 - 3.2 mm. The sample with the highest grinding energy has the highest percentage of fibre fragments between 0 - 0.2 mm in length. This suggests that increasing grinding energy causes large fibres to be cut into smaller fragments, which is consistent with the optical microscope images in Figure 5.2. Padberg and co-authors used a fibre image analyser to study the morphology of MFC produced using a Supermasscolloider. The study found a decreased percentage of the length weighted distribution of fibre fractions between 0.2 - 1.2 mm in length with increasing number of passes through the Supermasscolloider and an increased percentage of fibre fractions between 0.01- 0.2 mm in length.⁵⁸ This trend is similar to the results shown in Figure 5.5 except the MFC used in the present study may have been

coarser since large fragments are present above 1.2 mm which were not present in the work of Padberg and co-authors.⁵⁸

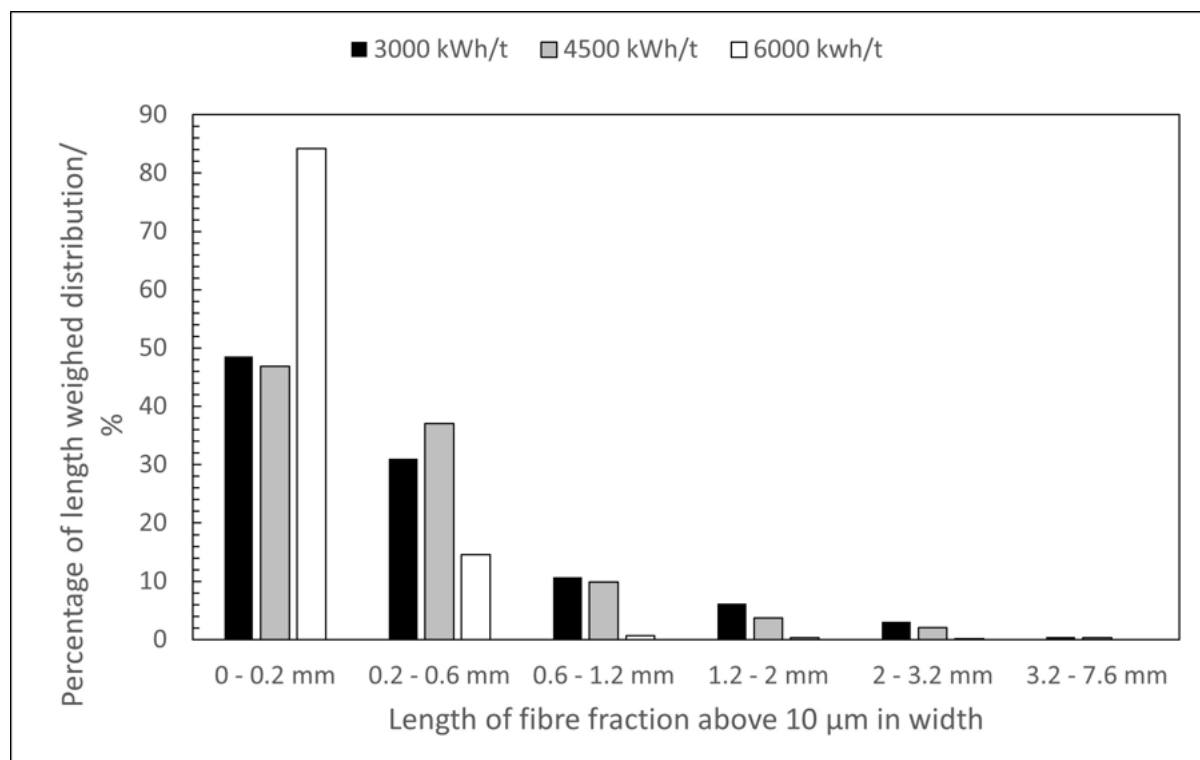


Fig. 5.5. Percentage of length weighted distribution of MFC with increasing grinding energy above 10 µm in width in length fractions ranging from 0 - 7.6 mm

Figure 5.6 shows the same information for MFC produced with increasing homogenisation pressure. In the case of homogenisation, there are only small differences when increasing the pressure on the percentage of fibre fragment lengths, suggesting that the homogenisation process does not reduce length of large fibre fragments.

Figure 5.7 shows the Fines A and Fines B of refined, ground and homogenised cellulose samples used in the study. Increasing pulp refining increases both Fines A and Fines B. This suggests that fine cellulose fibres were released from the fibres throughout the refining process. Increasing grinding energy has a large effect on increasing Fines A and also increasing Fines B. Padberg and co-authors found that as the number of passes through a Supermasscolloider grinder increased, the Fines A content of the MFC increased.⁵⁸ Figure 5.2 shows that increasing grinding energy results in significant fibrillation of the fibres and separation of fibrils from the main fibre. Additionally, when grinding energy was increased to 6000 k W h t⁻¹, there is a visible shortening of fibrils which could explain the high Fines A observed. Increasing homogenisation pressure increases Fines A but there is no overall increase or decrease in Fines B throughout the pressure series. However, it is apparent that the homogenised samples have a significantly higher Fines B than the ground samples. In Figure 5.3, finely dispersed, long cellulose fibrils are observed.

FLT Indices

For paper with relatively low fibre bonding, tensile failure occurs with minimal breaking of fibres. For paper with relatively high fibre bonding, tensile failure occurs with many broken fibres. Both the strength of the fibres and the degree of bonding are important to the tensile strength index of paper. The Page equation (Equation 5.1) describes the relationship between tensile strength, fibre strength and bonded area where Z is the zero span tensile, a test which

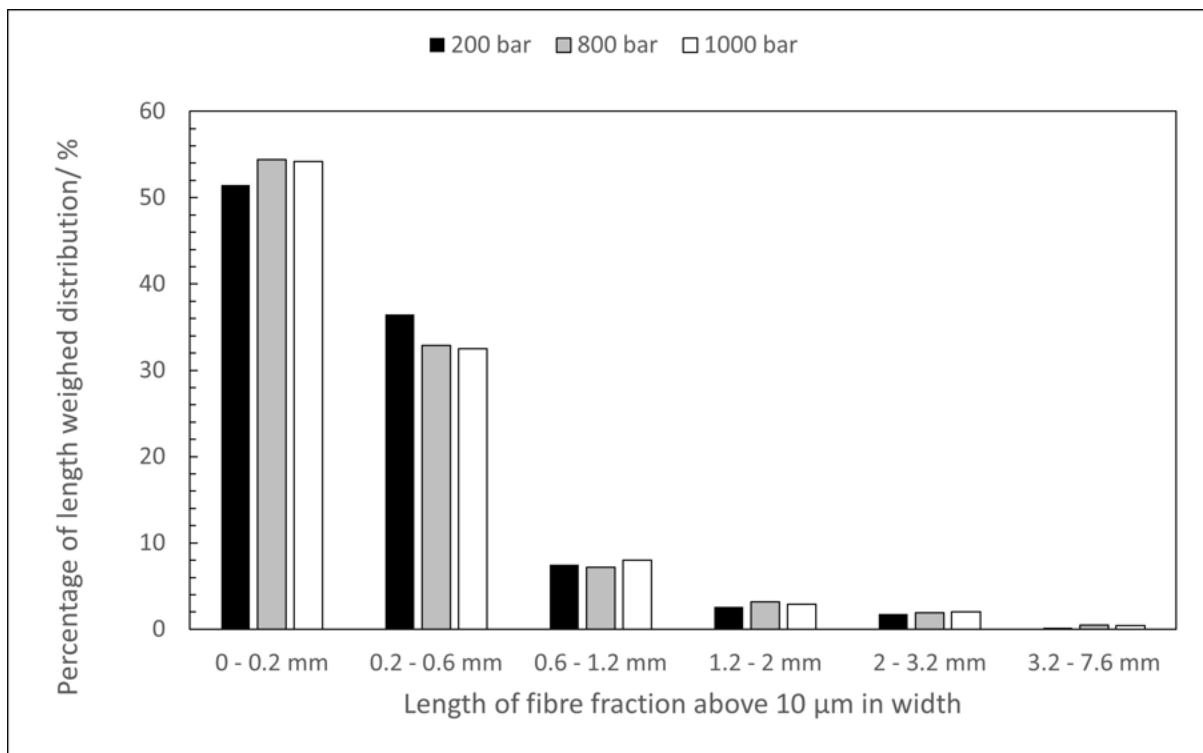


Fig. 5.6. Percentage of length weighted distribution of MFC with increasing homogenisation pressure above 10 µm in width in length fractions ranging from 0 - 7.6 mm

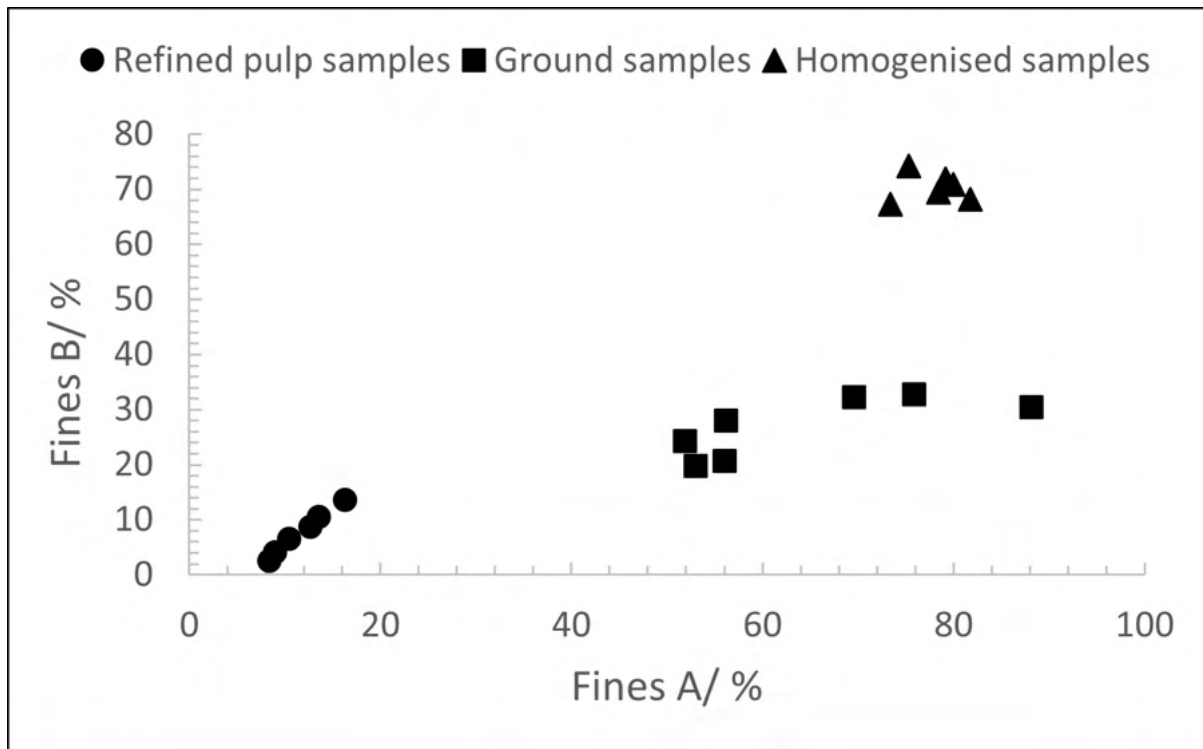


Fig. 5.7. Fines A and Fines B of refined, ground and homogenised cellulose

measures strength of fibres; A is the cross sectional area of a fibre; ρ is the fibre density; b is shear bond strength; L is the length of fibres; P is the perimeter of a fibre cross section and RBA is the relative bonded area of fibres. The first term in the Page equation represents breakage of fibres and the second breakage of bonds.^{122,166,167} Whether tensile failure occurs

at the fibres due to a lack of joint strength or at bonds between fibres depends on the relative size of the terms in the Page equation, or the balance between the bonding strength compared to the fibre strength.¹⁶⁶

$$\frac{1}{TSI} = \frac{9}{8} \times \frac{1}{Z} + \frac{12A\rho}{\tau_s PL(RBA)} \quad (5.1)$$

Taylor and co-authors suggested that the MFC-mineral composite paper made in the FLT test should conform to the Page equation.¹⁶⁸ As fibres are processed into MFC, relative bonded area within the sheet increases. Therefore, the second term in the Page equation would decrease in size, meaning that tensile strength of sheets would be highly influenced by strength of fibres or fibrils. The FLT test involves making sheets of 20 wt% MFC and 80 w% calcium carbonate. Therefore, the bonded area of the sheet is significantly decreased compared to a sheet made from only MFC, increasing the size of the second term in the Page equation. This means that the tensile strength fails through breakage of bonds rather than fibres or fibrils.^{113,168}

Figure 5.8 shows how the FLT index of the cellulose changed through the refining, grinding and homogenisation processes. Increasing level of refining results in an increase in FLT index. Initially, increasing grinding energy results in an increase in FLT index, followed by a decrease. The MFC sample produced at 4000 k W h t⁻¹ showed a comparatively low FLT index compared to other samples. Later in the study when films of the MFC were made, it was apparent that there was a high proportion of dried MFC in the material, which may have been present also when the FLT was measured, therefore resulting in a lower value. As homogenisation pressure increased, there was an increase in FLT index, followed by a decrease after 800 bar. It was unclear why this decrease may have occurred, but could be because of degradation of the cellulose at high homogenisation pressures or a reduction in fibril length may have occurred. When a network of cellulose fibres are dried, they are drawn into close proximity by surface tension forces from evaporating water. Increasing fibrillation of fibres allows for more contact between fibrils and fibres during this stage which can then be drawn into close contact as the web dries. As the fibres are drawn into close contact from capillary forces, hydrogen bonds and dispersion forces form between fibres.^{115,169} Several studies have found that sheets made from MFC have a higher tensile strength than those from pulp or refined pulp. This is thought to be due to increased surface area of the cellulose forming an entangled network with many hydrogen bonds.^{170–172} Nair and co-authors found that increasing the fibrillation time of cellulose pulp using a Supermasscolloider initially increased tensile strength of sheets until a plateau was found. Increase in strength was linked to an increase in density of the sheets and explained as a result of increased cellulose surface area and bonding, therefore increasing bond strength and bonded area.¹⁷³ Wohlerlert and co-authors suggest that hydrogen bonding is not the dominant mechanism of paper strength and instead other intermolecular forces and physical entanglement govern the strength of paper materials.⁷⁴ However, increasing the fibrillation of fibres is still likely to affect strength by increasing surface area to allow for greater entanglement and bonding.

Figure 5.8 shows that refining pulp increases tensile strength of the mineral-MFC sheets, likely to due an increase in bonded area as a result of increased cellulose surface area allowing more bonds and entanglements to form within the sheet. The MFC produced through grinding makes FLT sheets with a much higher tensile strength index than refining and this tensile strength is further increased by homogenisation.

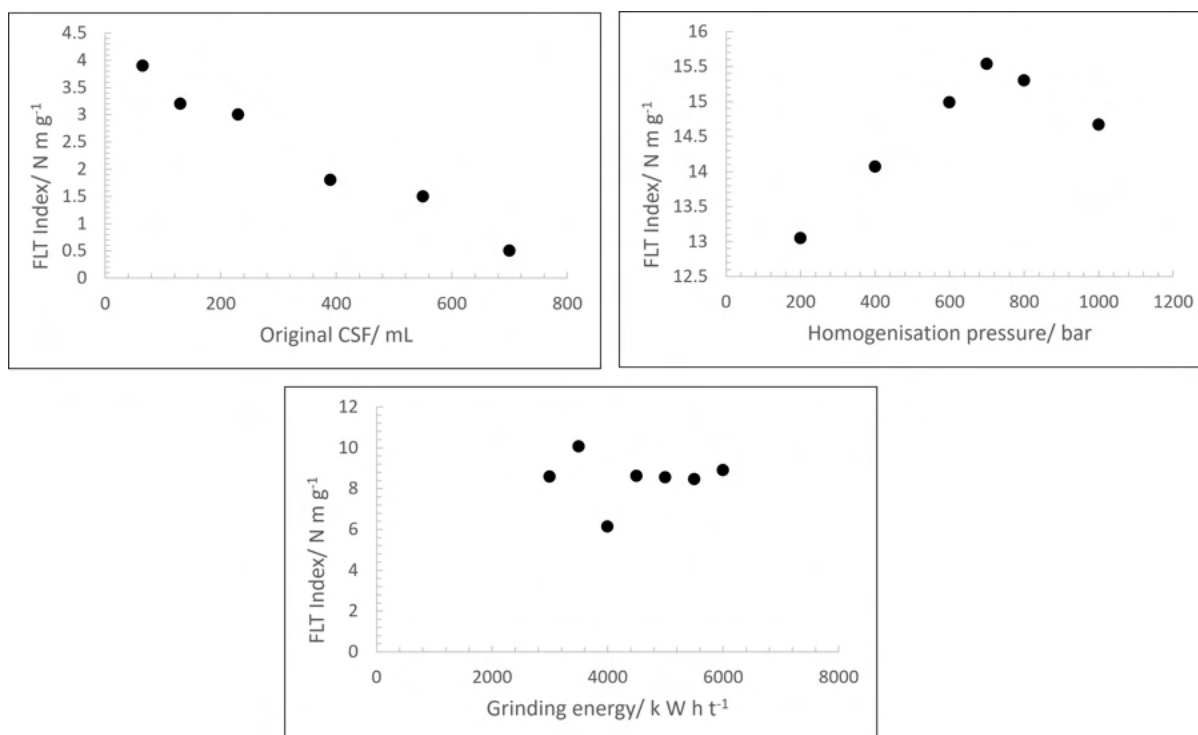


Fig. 5.8. Effect of increasing refining, grinding energy, or homogenisation pressure on the FLT index- the tensile strength index of a sheet made from 80 wt% mineral and 20 wt% MFC.

5.3.2 Crystallinity Indices of Refined Pulp Sheets and MFC Films

Crystallinity Index Calculated from XRD Data

CrystalDiffract software was used to remove a background from the XRD spectra. An example of an XRD spectrum for an unrefined pulp sheet is shown in Figure 5.9 with the Miller indices of peaks labeled as seen in the work of Park and co-workers.⁵⁷

The XRD measurements were performed on cellulose films. Therefore, the sample may not be oriented randomly, as would usually be the case in quantitative powder diffraction experiments. This orientation of the films may have altered the ratio of the diffraction peaks used to calculate crystallinity index of cellulose.⁵⁷ Han and co-authors found that films made from enzyme treated MFC showed that the crystalline axis running along the cellulose chains was planar to the film.¹⁷⁴

Figure 5.10 shows the powder diffraction pattern for the sheet made from unrefined pulp alongside a literature powder diffraction trace for cellulose

I/β . The powder diffraction trace was taken from the crystal structure of cellulose I/β provided by Nishiyama and co-authors (Supporting Information).¹⁷⁵ Free Mercury software was used to load the crystal information file and produce a powder diffraction trace (Mercury 4.0: from visualization to analysis, design and prediction)¹⁷⁶. For the unrefined pulp sheet measured from the current study, the ratio between the intensity of the 101 and 002 peak was 1:2. For the literature powder diffraction trace, the ratio was 1:3. This difference could be caused by orientation effects in the sheet, which may influence calculation of the Segal crystallinity index. However, all samples were measured as films which suggests that any orientation effects should be equivalent across the cellulose samples.

Table 5.2 shows the results of the calculations of the Segal crystallinity index for cellulose, calculated using Equation 3.15.¹⁴⁷ There is a slight increase in CrI between the unrefined and refined pulp sample. There is a decrease in crystallinity index of the MFC samples compared to

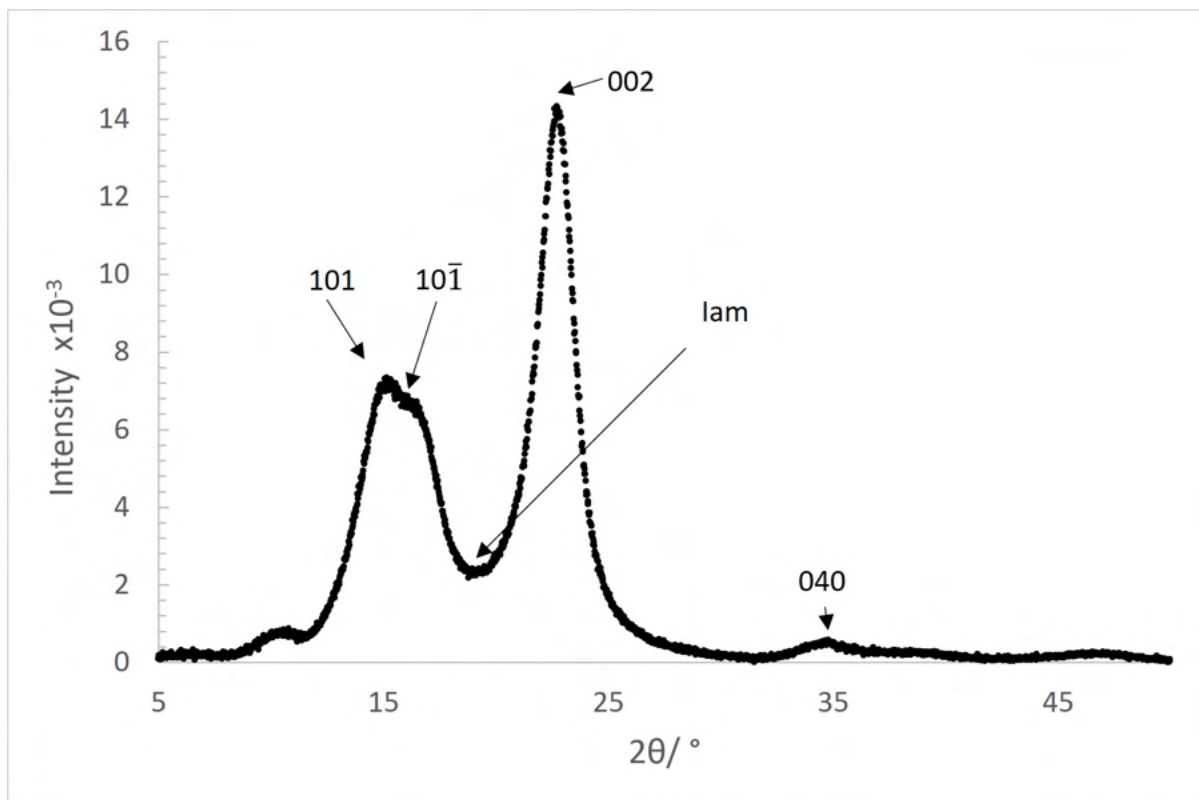


Fig. 5.9. XRD diffraction pattern for unrefined pulp with background removed with Miller indices of peaks labelled and the amorphous intensity (lam) used in the Segal crystallinity index calculation labelled

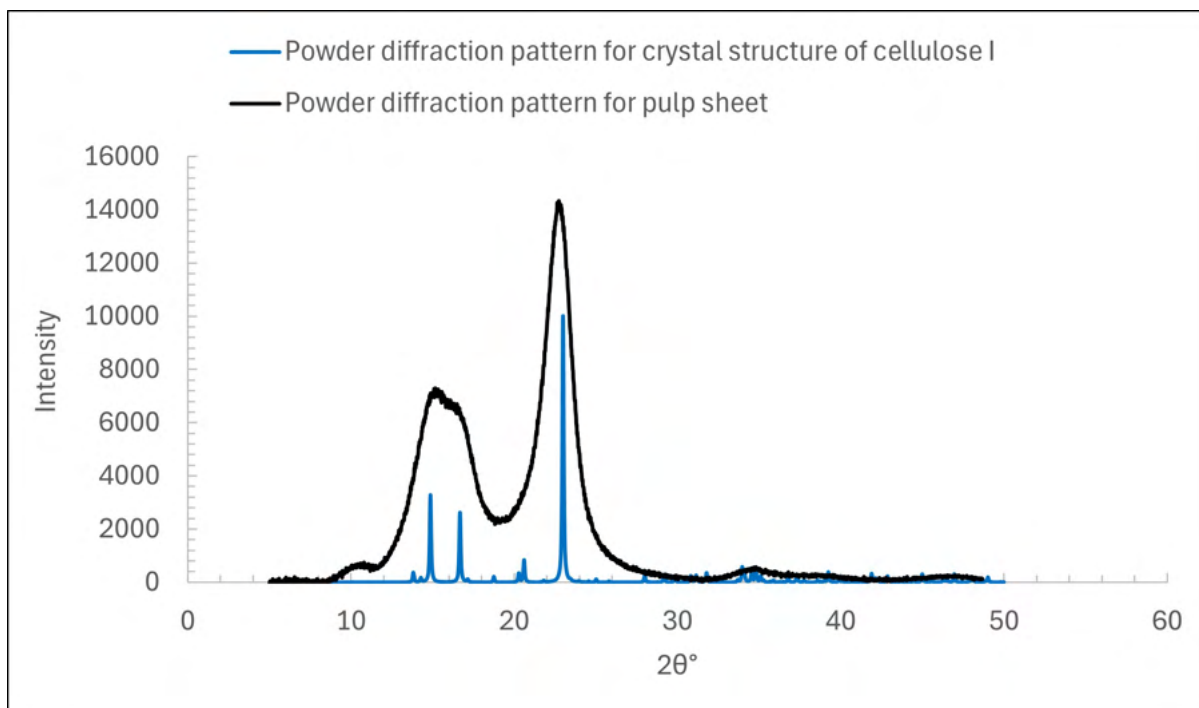


Fig. 5.10. XRD diffraction pattern for unrefined pulp with background removed and literature powder diffraction pattern for cellulose from Nishiyama and co-authors¹⁷⁵

the unrefined pulp and 65 CSF pulp samples. This suggests that the grinding process resulted in some degradation to the cellulose crystallinity. Similarly, there is a decrease in crystallinity

Sample	$2\theta I_{002}^{\circ}$	$2\theta I_{am}^{\circ}$	CrI %
Unrefined pulp	22.71	19.24	83.62
65 CSF pulp	22.73	19.21	84.48
3000 k W h t ⁻¹ MFC	22.65	19.25	79.64
4000 k W h t ⁻¹ MFC	22.65	19.21	81.73
6000 k W h t ⁻¹ MFC	22.65	19.13	78.56
4000 k W h t ⁻¹ + 400 bar MFC	22.65	19.13	78.37
4000 k W h t ⁻¹ + 1000 bar MFC	22.65	19.13	76.97

Table 5.2

Crystallinity indices of cellulose sheets, calculated from XRD data using the Segal method.

index when the MFC sample is homogenised and a further decrease when the homogenisation pressure is increased. These values for crystallinity index are in a comparable range to those calculated for different cellulose samples by Park and co-authors (76– 85% current work vs 78–95% calculated by Park and co-authors). However, these values may be higher than the true value due to orientation effects from measuring the samples as films as opposed to powders and that the Segal peak height method can cause an overestimation of the crystallinity due to the amorphous cellulose contributing to the 002 peak height.⁵⁷

For the calculation of the Ruland-Vonk crystallinity index, the XRD trace for the guar gum was plotted alongside the trace of the unrefined pulp sheet. A scale factor was applied to the guar gum trace so that there were no areas where the intensity was higher than the cellulose trace. The factor that was chosen for this purpose was to divide the entire guar gum spectrum by 20. To calculate the crystallinity index, the area of the amorphous material– the area under the scaled guar gum trace– was subtracted from the XRD spectra of the cellulose materials. The fraction of crystalline material relative to the total area under the cellulose curve was calculated according to Park and co-authors.⁵⁷ Table 5.3 shows the crystallinity indices of the cellulose sheets calculated using the Ruland-Vonk method. In contrast to the work of Park and co-authors, the crystallinity index calculated from the Ruland-Vonk method is higher than the Segal crystallinity index calculated.⁵⁷ This may have been due to the use of guar gum to produce the amorphous cellulose trace, which could have been an improper representation of amorphous cellulose. Also, a scale factor was necessary to bring the guar gum trace below that of the cellulose, which may have led to an underestimation of the amorphous contribution to the cellulose diffraction peak.

There are some similarities to Table 5.2, as there is a small increase in crystallinity index between the unrefined pulp sheet and the 65 CSF pulp sheet. There is also a decrease in crystallinity index between the refined pulp sample and the MFC samples, again suggesting that the grinding process causes some deterioration in the crystallinity of the cellulose.

Overall, the XRD data from Table 5.2 and Table 5.3 suggest that there may be a small decrease in crystallinity index when grinding at high energy or homogenising at high pressure.

Padberg and co-authors observed a decrease in crystallinity index of cellulose measured using XRD as the number of passes through a Supermasscolloider increased.⁵⁸ However, Siró and co-workers found no change in the crystallinity index of cellulose films measured using XRD when the number of passes through a homogeniser was increased to make the MFC.⁹¹ Spence and co-authors also investigated the effect of refining and homogenising on the crystallinity index of cellulose films measured through XRD and found a slight increase in crystallinity when cellulose was refined and a small decrease after homogenising.¹⁷⁷ The effect of mechanical treatment on cellulose crystallinity appears to vary significantly with the method and intensity

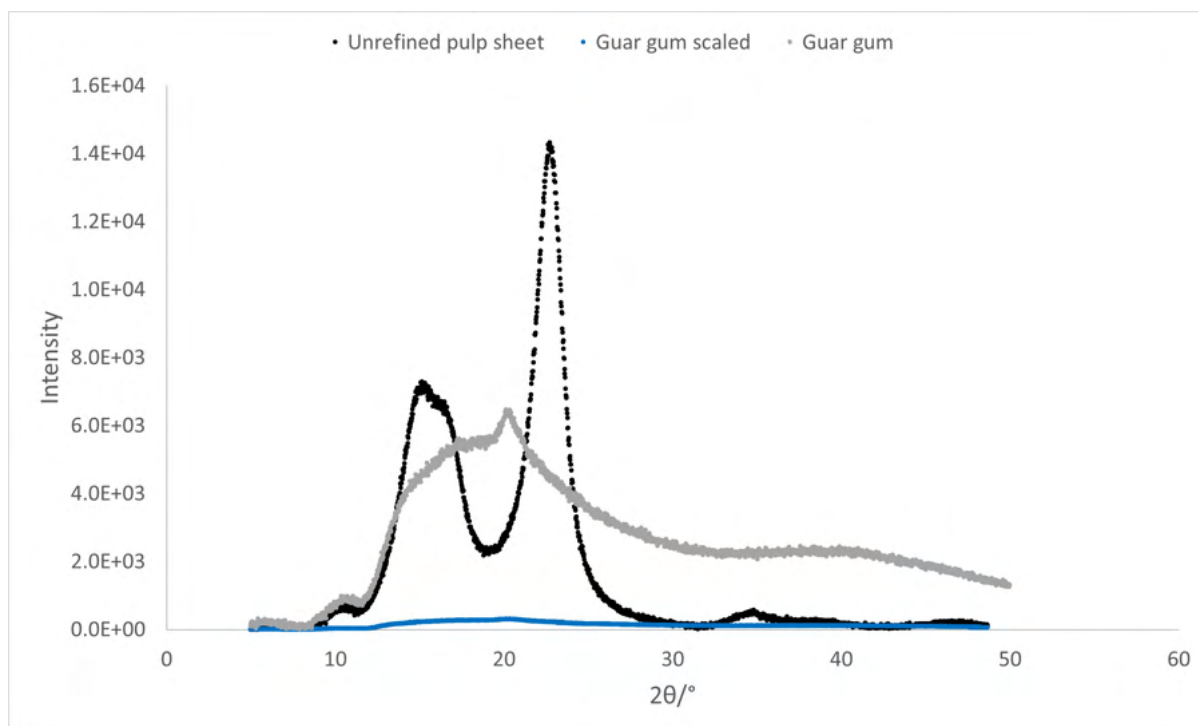


Fig. 5.11. XRD patterns of guar gum in reference to cellulose sheet

Sample	Ruland-Vonk CrI %
Unrefined pulp	92.37
65 CSF pulp	92.50
3000 k W h t ⁻¹ MFC	91.20
4000 k W h t ⁻¹ MFC	90.93
6000 k W h t ⁻¹ MFC	90.87
4000 k W h t ⁻¹ + 400 bar MFC	91.57
4000 k W h t ⁻¹ + 1000 bar MFC	91.23

Table 5.3

Crystallinity indices of cellulose sheets, calculated using method described by Park and co-authors⁵⁷.

of the treatment. The difficulty in quantitative interpretation of cellulose crystallinity may also contribute to differences in the effect of mechanical treatment between different studies.

Crystallinity index calculated from ATR- FTIR data

Nelson and O'Connor were used Equation 3.16 and Equation 3.17 to calculate crystallinity indices of cellulose ground into KBr pellets from ratios of FTIR absorbance intensities.^{153,154} Figure 5.12 shows the FTIR spectrum measured in ATR mode of a sheet made from unrefined pulp. The peak height measuring tool on the OMNIC software was used to measure heights of the peaks needed for the crystallinity index calculations. For the peaks at 1430 cm⁻¹ and 893 cm⁻¹ it was unclear where the peak should be measured as there appeared to be a smaller peak as part of a larger peak. For the peak at 1430 cm⁻¹, the smaller peak height value was chosen as there was a defined second peak. For the peak at 893 cm⁻¹, the entire peak was chosen to fit a base line to calculate peak height because there was only a small bump in the peak which was much less defined and was not present for some samples. Table 5.4 shows the crystallinity indices calculated from the FTIR data. There is little agreement between Cr1 and

Sample	Cr1- 1372/2900	Cr2- 1429/893
Unrefined pulp	0.60	0.73
65 CSF pulp	0.64	0.75
3000 k W h t ⁻¹ MFC	0.5	0.63
4000 k W h t ⁻¹ MFC	0.57	0.59
6000 k W h t ⁻¹ MFC	0.71	0.44
4000 k W h t ⁻¹ + 400 bar MFC	0.64	0.42
4000 k W h t ⁻¹ + 1000 bar MFC	0.71	0.5

Table 5.4

Crystallinity indices of cellulose sheets, calculated using FTIR peak height ratios.

Cr2. However, Cr2 follows the trend from the Segal and Ruland-Vonk analysis of the XRD data where there is a decrease in crystallinity index between refined pulp and MFC, particularly when a higher grinding energy is used. The inconsistent results for the FTIR crystallinity index Cr1 could be due to the original literature method using a KBr- cellulose pellet for the FTIR analysis and not ATR-FTIR directly on the surface of a cellulose film.

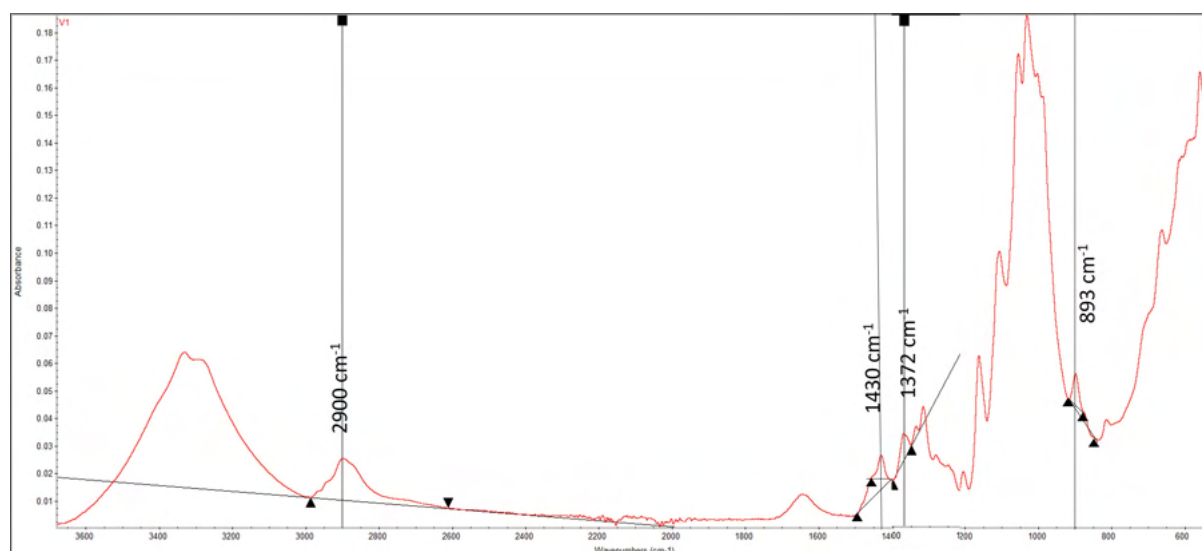


Fig. 5.12. FTIR spectra of sheet made from unrefined pulp measured using ATR mode, showing measurement of peak heights for peaks used in crystallinity index calculations.

5.3.3 Surface Characterisation of Coated Sheets

The topography of the cellulose coated sheets was visualised using a laser interferometric profilometer. Images of the height profiles of refined pulp coated onto the base sheet are shown in Figure 5.13. As the CSF decreased from 550 CSF to 65 CSF, there was a considerable decrease in the porosity of the coated cellulose layer and discrete fibres seen in the 700 and 550 CSF films appear to bond together into a smoother network.

Figure 5.14 shows the height profile images of base sheets coated with MFC made with increasing grinding energy. Overall, the sheet surfaces were smoother with fewer large fibre fragments visible in the coating layer than the sheet coated with 65 CSF pulp. This may be linked to the more fibrillated fibre structure observed for the ground MFC material than the refined pulp material in Figure 5.2. The number of large fibres in the images appears to begin

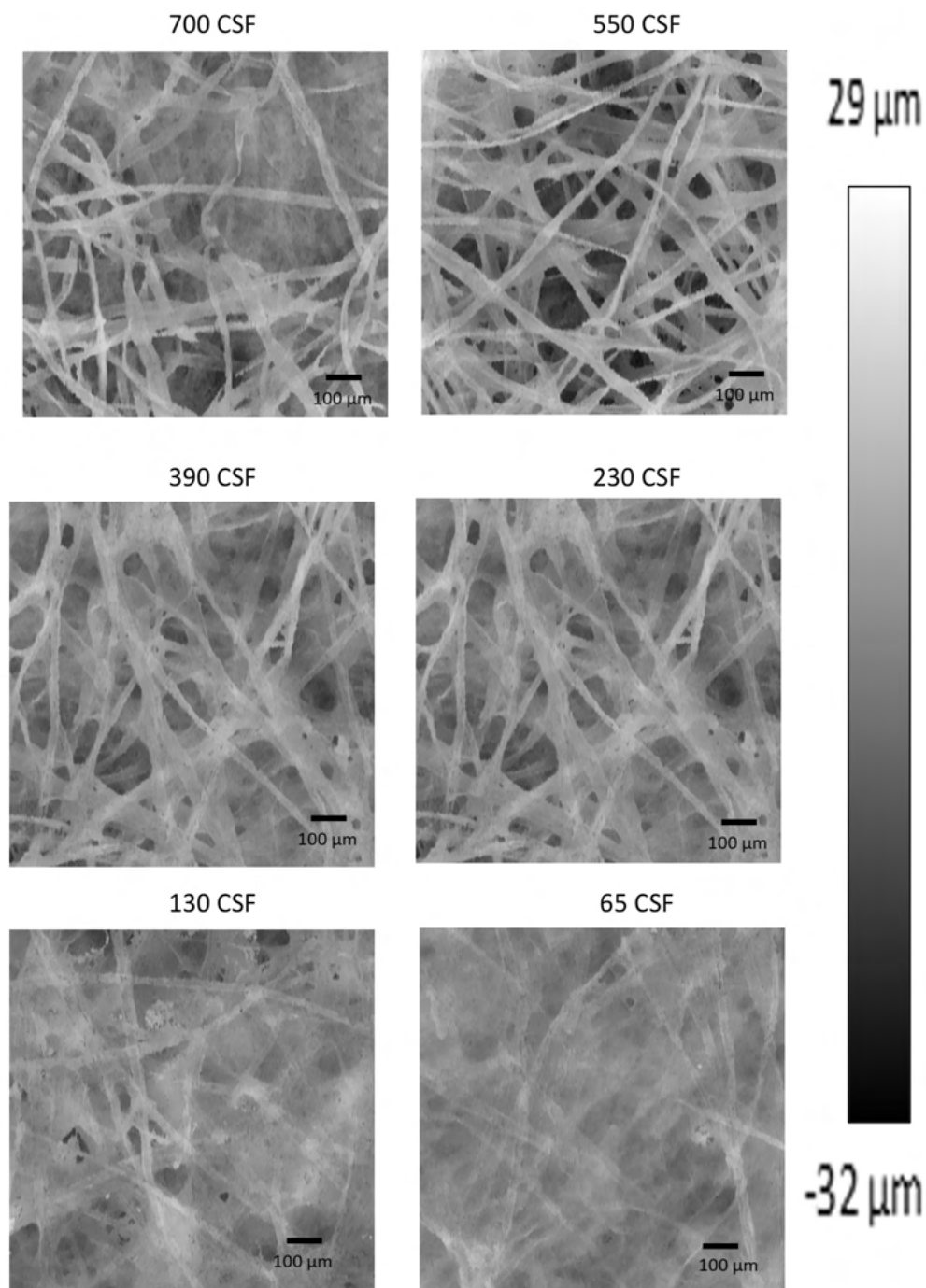


Fig. 5.13. Height profile images of base sheets recorded coated with refined pulp using an interferometric laser profilometer.

to decrease after $4500 \text{ k W h t}^{-1}$ which supports the fibre image analyser results that the number of longer fibre fragments decrease as the grinding energy increases.

Figure 5.15 shows that the sheets coated with ground and homogenised MFC had a smooth surface although in some cases there is evidence of larger fibres disrupting the MFC layer which further suggests that the homogenization process does not eliminate large fibre fragments, as shown in the fibre analyser data in Figure 5.6. At 800 and 1000 bar, no fibre fragments are visible. This could be because the laser height profile images cover a relatively small surface

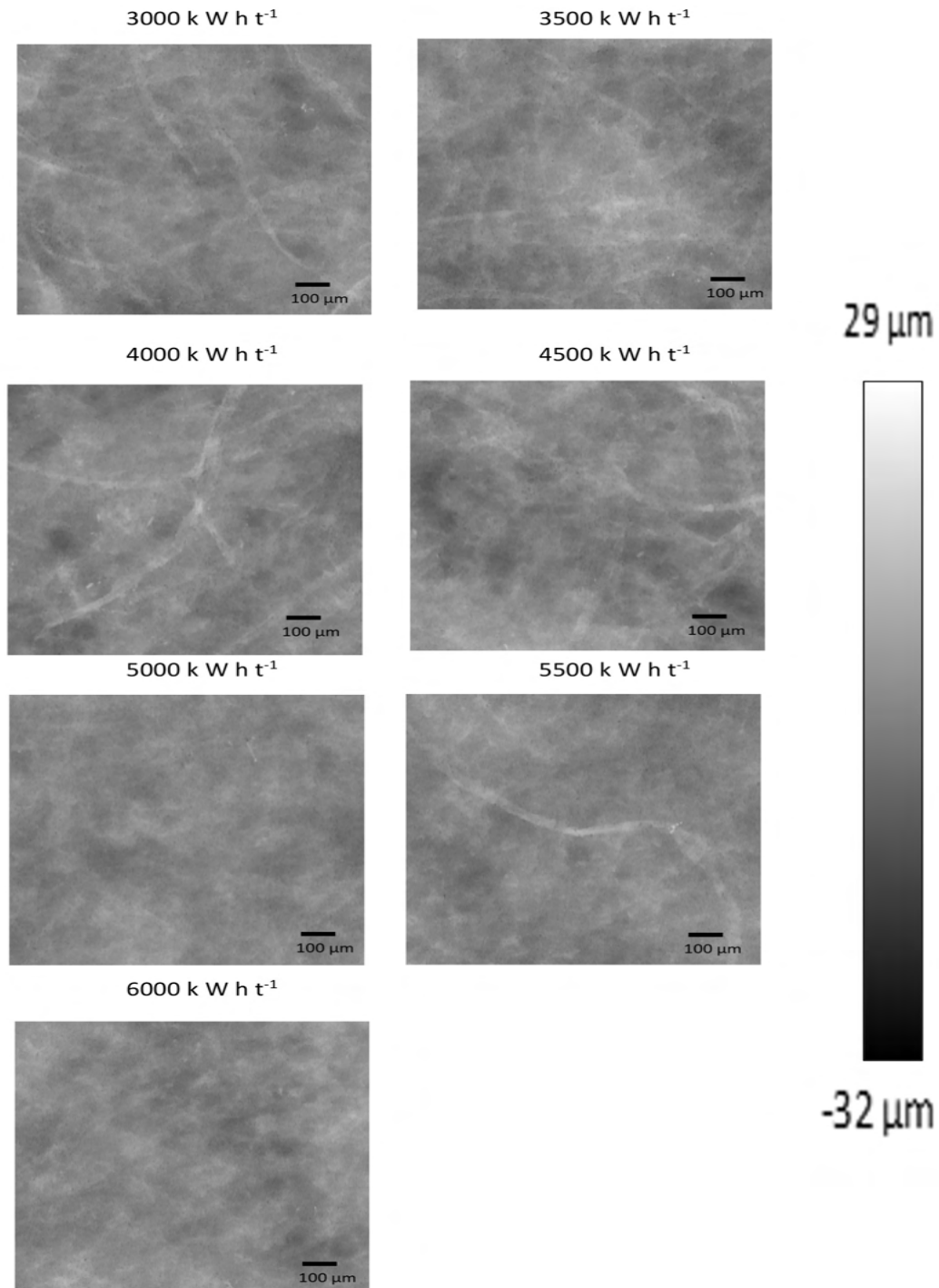


Fig. 5.14. Height profile images of ground MFC coated base sheets recorded using an interferometric laser profilometer.

area of 1.05 mm^2 and it may be that by chance no large fibre fragments were present in this area. However, it could also be the case that the increased cellulose fibrillation allowed the large fibre fragments to be incorporated into the layer without causing a disruption as there were many fine fibrils to fill in gaps around the large fibres.

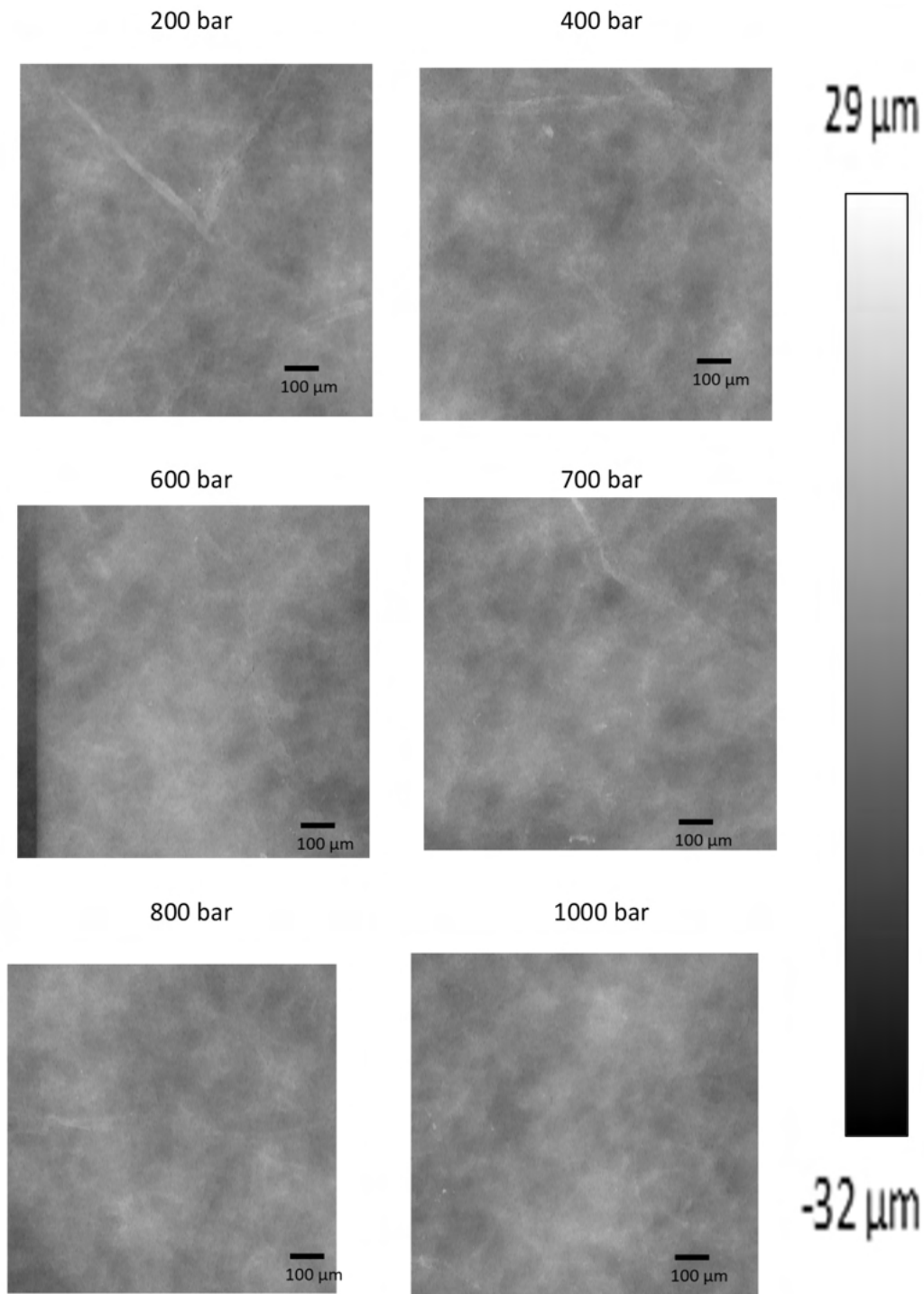


Fig. 5.15. Height profile images of ground and homogenised MFC coated base sheets recorded using an interferometric laser profilometer.

5.3.4 Air Permeability of Cellulose Coated Sheets

Figure 5.16 shows the effect of increasing level of refining, grinding energy and homogenisation pressure on the Bendtsen porosity of base sheets coated with 10 g m^{-2} of cellulose. Bendtsen porosity steadily decreases as CSF decreases. Increasing level of refining can increase the density of sheets because fibres form a more closely packed network and fines produced from the refining can fill in gaps between fibres.¹⁷⁸ The Bendtsen porosity of the sheet coated with 65 CSF refined pulp was considerably higher than the Bendtsen porosity of any of the MFC coated samples. When comparing Figure 5.1 with Figure 5.2, it is apparent that the MFC sample contained considerably more liberated fibrils and less larger fibre fragments than the 65 CSF pulp which could explain why the MFC was able to form a less porous layer as the material could pack together more efficiently and form more hydrogen bonds.

The MFC sample produced at $4500 \text{ k W h t}^{-1}$ formed a layer with a higher air permeability than any of the other MFC samples. This corresponds with the lower FLT value for this sample shown in Figure 5.8 and may be due to the presence of dried MFC which was visible later in the study when films of the material were made. Despite some variation in the results, the homogenised MFC samples all gave a Bendtsen porosity value of 0, indicating that the sensitivity limit of the Bendtsen porosity instrument had been reached.

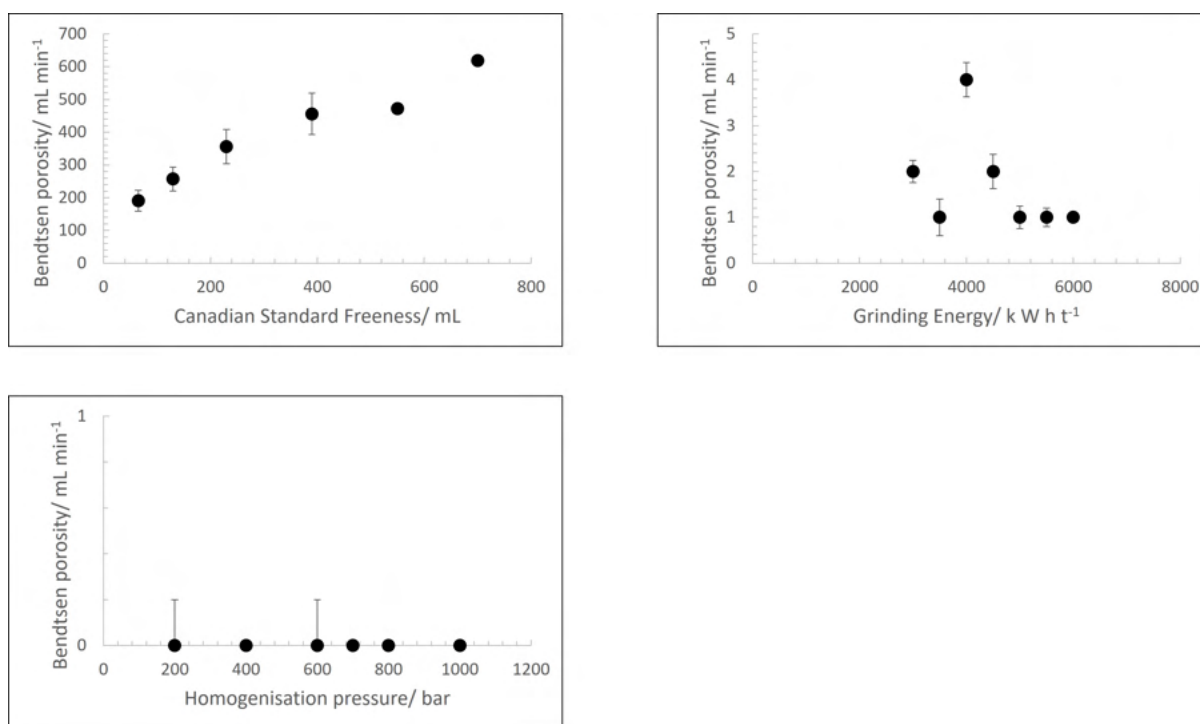


Fig. 5.16. The effect of increasing refining, increasing grinding energy and increasing homogenisation pressure on the Bendtsen porosity of base sheets coated with 10 g m^{-2} of cellulose through vacuum filtration.

5.3.5 Grease Resistance of Cellulose Coated Sheets

Figure 5.17 shows the Kit number of the MFC coated sheets. Kit was also measured for sheets coated with refined pulp samples but all samples failed Kit number 1, showing that they had no grease resistance. This indicated that the network formed by refined pulp contained enough porosity to allow wicking of oil through the network. The sheets coated with MFC all showed improved barrier properties compared to the sheets coated with refined pulp. This

could be related to the smoother, more compact structure of the MFC layer shown in the laser topography images compared to the refined pulp samples. There was an overall increase in Kit number as the grinding energy of MFC increased. Grease resistance also increases as the homogenisation pressure increases, reaching the maximum grease resistance measurable in the test at 700 bar. This suggests that a change occurring during the homogenisation process was beneficial to the grease barrier properties of MFC layer.

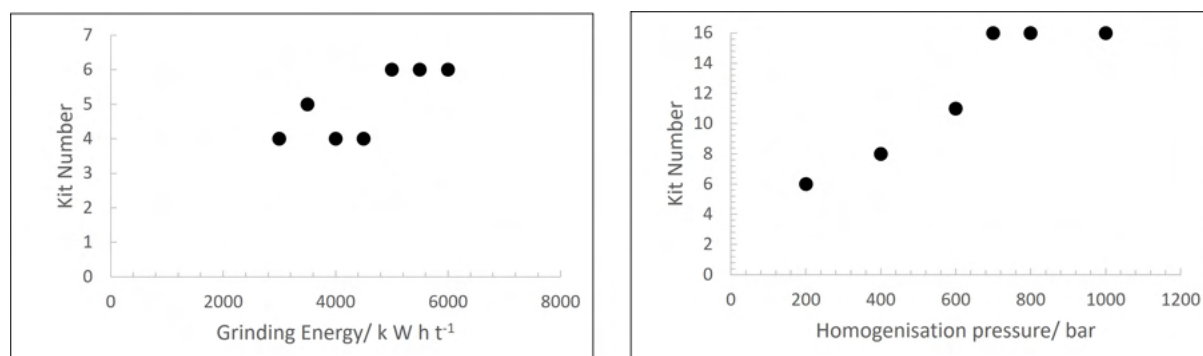


Fig. 5.17. The effect of increasing grinding energy and increasing homogenisation pressure on the grease resistance of base sheets coated with 10 g m^{-2} of cellulose through vacuum filtration. Increasing Kit number corresponds with increasing grease resistance

A summary of fibre analyser parameters that continuously increase or decrease as homogenisation pressure increases is shown in Table 5.5. Lc(n) decreasing below 0.2 mm and increasing Fines A both refer to an increase in the production of particles shorter than 0.2 mm . A corresponding decrease in fibrillation could imply that increasing the homogenisation pressure results in short fibrils previously attached to the fibres being removed and released as short fines. Increasing F1 (l) and F2 (l) imply that there is an increase in small fibre fragments being produced, although this is a smaller effect than seen for grinding. Changes to the kink and curl suggest that the homogenisation process results in changes to the sharp bends and curls within fibres with a width greater than $10 \text{ }\mu\text{m}$.

Figure 5.18 shows the effect of the parameters listed in Table 5.5 on the Kit number recorded for ground and homogenised MFC samples. F1(l) and F2(l) are not included because grinding has a much greater effect than homogenising in cutting large fibre fragments as seen in Figure 5.5 and Figure 5.6 but increasing grinding energy did not greatly increase Kit number. Fines A and Curl show the strongest correlations with Kit number with increasing Fines A and decreasing Curl being favourable. The fibre image analyser uses optical imaging which means there may be many fibrils within the cellulose suspension that are too small to be included in the analysis. These small fibrils are likely to also be important to the barrier properties.

5.3.6 Heptane Vapour Barrier of Cellulose Coated Sheets

The HVTR of the 65 CSF coated sheet was $2146 \pm 134 \text{ g m}^{-2} \text{ day}^{-1}$ compared to $2353 \pm 59 \text{ g m}^{-2} \text{ day}^{-1}$ for the sheet which had only the water passed through in the filtration process. This shows that even the most heavily refined pulp sample provided only a slight improvement in oil vapour barrier. Figure 5.16 shows that there was a significant decrease in air permeability for a sheet coated with 65 CSF pulp. However, the HVTR results suggest that the network was still not compact enough to prevent enough diffusion of heptane vapour to be observed in the HVTR test.

Figure 5.19 shows the effect of increasing grinding energy or homogenisation pressure on the HVTR of MFC coated sheets. Firstly, it is apparent that grinding the MFC at 3000 k W h^{-1}

Parameter	Change
Lc(n)	Decrease
Curl	Decrease
Fines A	Increase
Fibrillation	Decrease
Kink 1/1000	Increase
Fines/ %	Increase
F1 (I) and F2 (I)	Increase
F4 Fibrillation	Decrease

Table 5.5

Fibre image analyser parameters that continuously increase or decrease as the homogenisation pressure increases

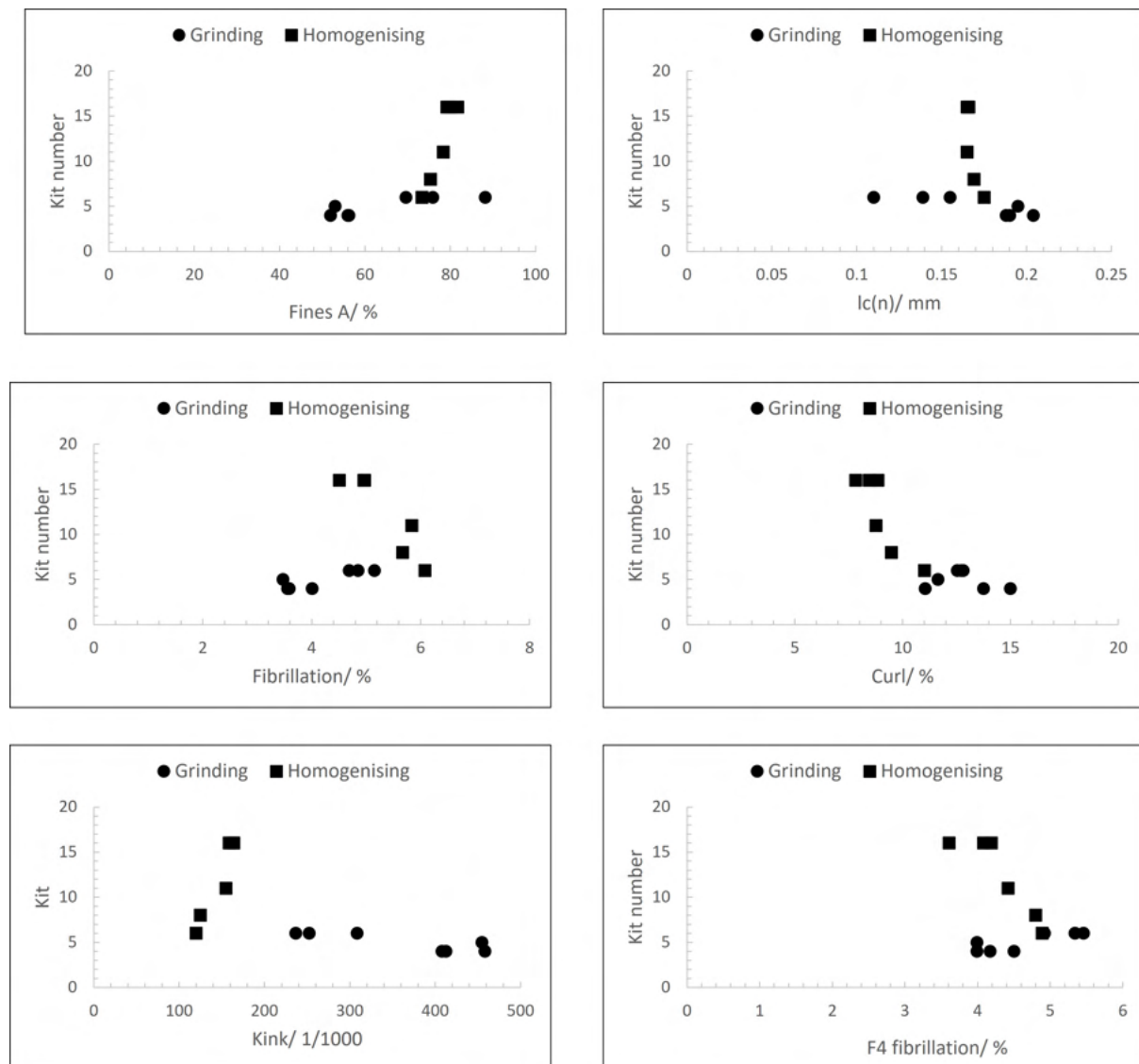


Fig. 5.18. The effect of changing fibre image analyser parameters that vary continuously with increasing homogenisation pressure on Kit number for ground and homogenised MFC samples.

creates a heptane vapour barrier. There is some variation in HVTR as the grinding energy increases but the most significant difference is between the ground and homogenised MFC samples. Homogenised MFC was a significantly better heptane vapour barrier although there was no further improvement in barrier properties when increasing the homogenisation pressure above 400 bar. Figure 5.7 shows that the homogenised samples had a significantly higher Fines B content than the ground samples. Figure 5.3 also shows that the homogenised MFC was more finely dispersed than that of the ground MFC. These observations suggest that these liberated, longer fibrils may be important for heptane barrier properties. Juntunen observed a decrease in hexane vapour transmission rate initially when increasing number of passes through a refiner to make MFC but this decrease plateaued when fibrillation was further increased.⁸²

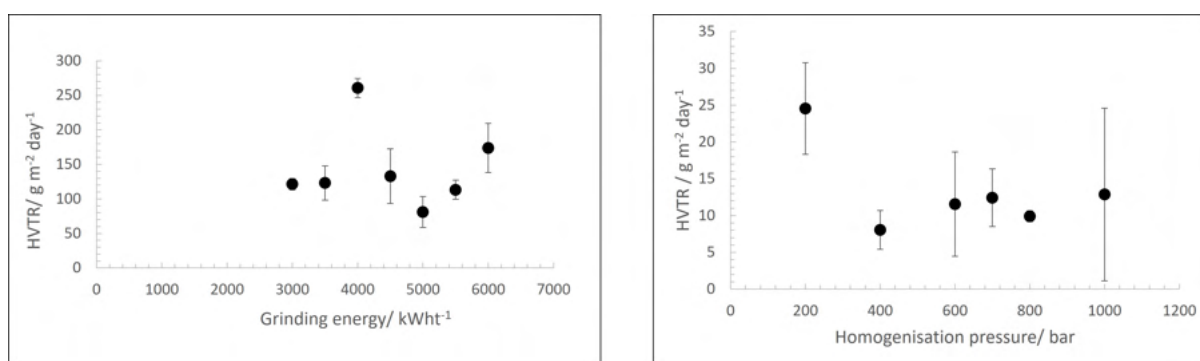


Fig. 5.19. The effect of increasing grinding energy and increasing homogenisation pressure on the HVTR of base sheets coated with 10 g m^{-2} of cellulose through vacuum filtration.

Figure 5.20 shows the relationship between Fines B and HVTR along with Fines A and Curl which were seen to be important for grease barrier properties. The data suggest that Fines A is not an important parameter for HVTR. For example, the samples produced through grinding which have high Fines A of 76% and 88% have a significantly higher HVTR than the MFC samples produced through homogenising, despite the Fines A being similar in both cases. Figure 5.20 suggests that Fines B and Curl may be important to HVTR. It is important to remember that the fibre image analyser uses optical imaging to characterise cellulose and therefore may be less effective at characterising the fine, homogenised material.

The Kit test is highly sensitive to small pinholes so Fines A may be more relevant in the Kit test because small cellulose fragments can fill in pinholes in the MFC layer. These small holes may have less of an impact on heptane vapour diffusion since this is an overall property of the layer and may therefore be less dependent on defects. Padberg and co-workers found that initially increasing the fibrillation of cellulose through increasing passes through a Supramasscolloider caused a sudden decrease in OTR to below the sensitivity level of the test.⁵⁸ This decrease in OTR was accompanied by an increase in Fines A from $41.77 \pm 0.36\%$ to $64.91 \pm 0.27\%$ and a decrease in the number of large fibre fragments. Figure 5.20 suggests that in the present study Fines A was not correlated with HVTR. This difference may be due to different methods being used to mechanically fibrillate the cellulose, leading to different changes in the morphology of cellulose as process intensity increased.

5.3.7 Relationship Between FLT Index and Barrier Properties

The FLT index is a quality control measure used by Fiberlean Technologies to assess MFC quality. A higher FLT index implies a greater bonding area and strength.^{152,168} It is reasonable to expect that increased bonded area in an MFC network facilitated through increased cellulose surface area should also improve barrier properties since increased density of an MFC network has

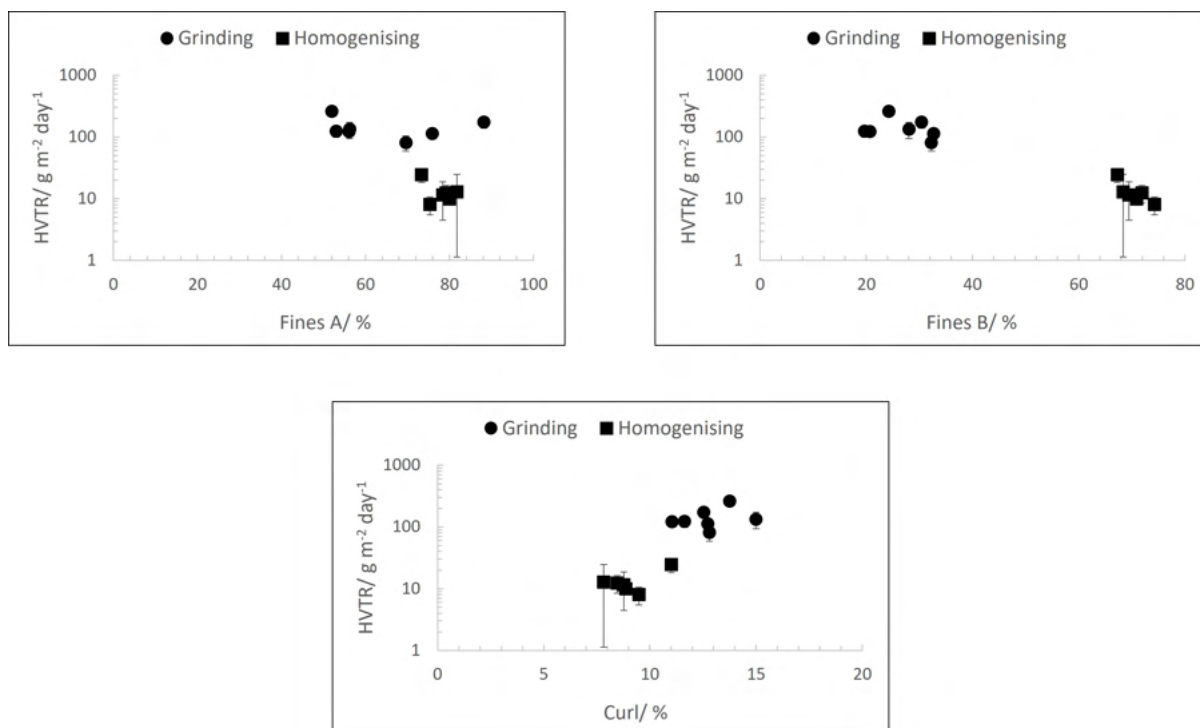


Fig. 5.20. The effect of fibre analyser parameters Fines A, Fines B and Curl on the HVTR of base sheets coated with 10 g m^{-2} of cellulose through vacuum filtration. HVTR is shown on a Log10 scale.

been related to increased strength.^{173,179–181} Therefore, the FLT index may give a quantitative indication of which MFC samples may form effective barrier layers.

Figure 5.21 shows how increasing FLT of refined pulp samples corresponds with a decrease in Bendtsen porosity of a layer of refined pulp coated onto base paper. This suggests that the FLT index may be a useful quantitative measure of how well a dense network of cellulose can form. The FLT index of the ground and homogenised MFC samples is related to grease resistance and HVTR in Figure 5.22. For these MFC samples, increasing FLT index appeared to correlate well with decreasing HVTR and increasing Kit number.

5.3.8 Morphology of Cellulose Sheets

Figure 5.23 shows optical microscope pictures of refined pulp sheets. The network of large overlapping fibres is apparent. The 65 CSF sheets show a smoother, denser network, with some porosity still remaining. Figure 5.24 shows images of the MFC sheets produced through ground MFC. There is a decrease in the appearance of large fibres when the grinding energy increases to $6000 \text{ k W h t}^{-1}$. This is in accordance with a decrease in large fibre fragments observed with increasing grinding in the fibre analyser data in Figure 5.5. Optical microscope images of sheets made from homogenised MFC are shown in Figure 5.25. Large fibre are clearly visible within the homogenised MFC sheets. However, this MFC made very effective barriers to heptane vapour and grease. This suggests that large fibres within the MFC may not be detrimental to barrier properties.

5.3.9 Density of Cellulose Sheets

Density of the 50 g m^{-2} sheets was calculated using sheet thickness measured using a digital micrometer. The effect of refining level, grinding energy, and homogenisation pressure on sheet

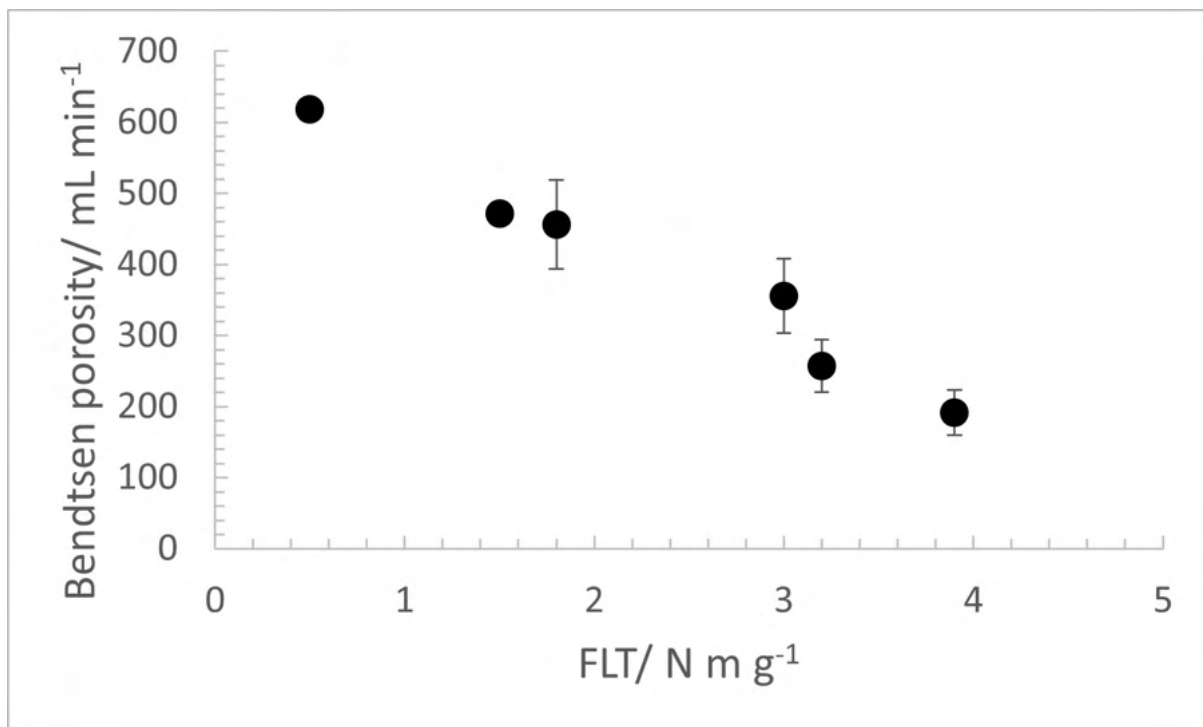


Fig. 5.21. Relationship between FLT index (tensile strength index of a 20:80 by weight sheet made from MFC and mineral) and Bendtsen porosity of coated sheets for refined pulp samples.

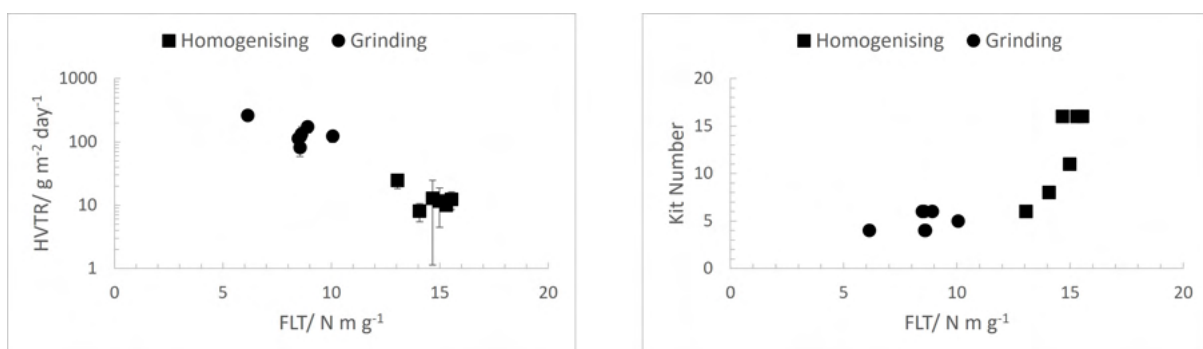
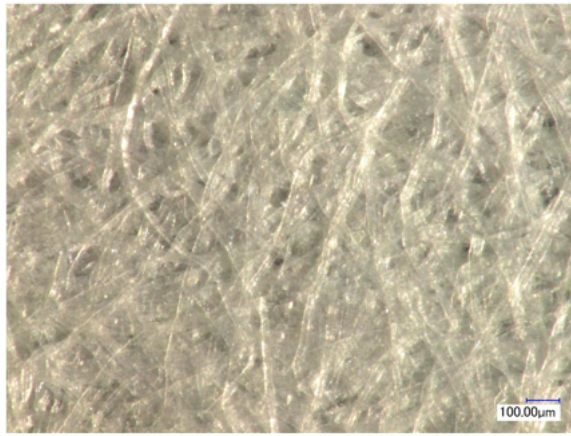
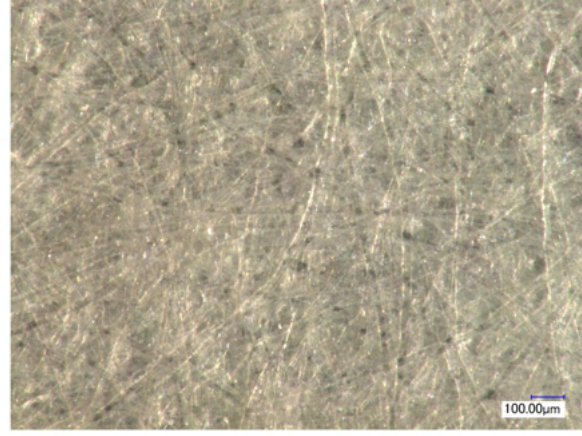


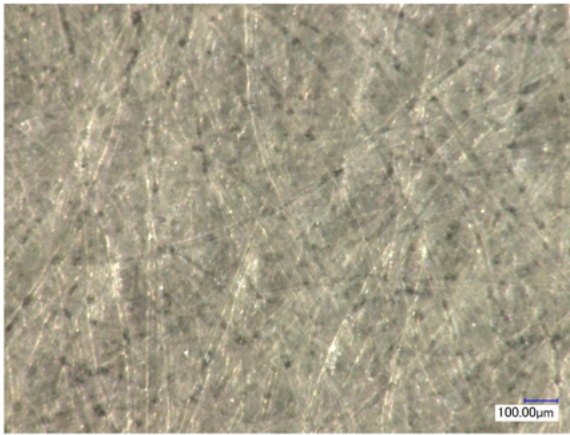
Fig. 5.22. Relationship between FLT index (tensile strength index of a 20:80 by weight sheet made from MFC and mineral), HVTR (shown on a logarithmic y axis), and Kit number of coated sheets.



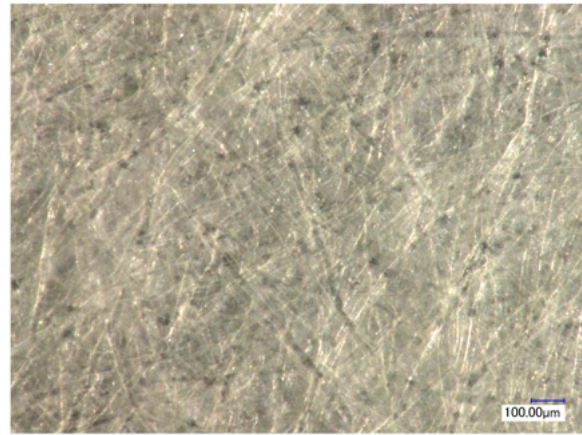
700 CSF



230 CSF



65 CSF- hand sheet former



65 CSF- vacuum filtration

Fig. 5.23. Optical microscope images of refined pulp sheets visualised in Reflectance mode using a Keyence microscope.



3000 kWh t⁻¹



4500 kWh t⁻¹



6000 kWh t⁻¹

Fig. 5.24. Optical microscope images of ground MFC sheets visualised in Reflectance mode using a Keyence microscope.



Fig. 5.25. Optical microscope images of homogenised MFC sheets visualised in Reflectance mode using a Keyence microscope.

density is shown in Figure 5.26. Decreasing CSF, corresponding with increasing refining time, resulted in an increase in density. Increasing grinding energy resulted in an overall increase in density and increasing homogenisation pressure led to an increase in density. An increase in density of a cellulose sheet implies that there is less pore space between the fibrils. Therefore, density of the cellulose sheets could be a simple way to predict barrier properties of MFC coatings. However, Figure 5.28 shows that there was no significant correlation between the density of a 50 g m^{-2} cellulose sheet and the HVTR or Kit number of a 10 g m^{-2} cellulose coating. This could be because the MFC coatings are significantly thinner than the sheets of cellulose and also made on a porous base sheet. Potentially, the MFC coating layer has a different density and structure than the MFC film due to an interface layer with the base sheet which may lead to greater connecting porosity in the thin MFC coatings compared to the MFC films where the density was measured. For further discussion on the measurement of density using a digital micrometer, please see Section 6.3.2.

5.3.10 Water Vapour Barrier Properties of Cellulose sheets

As described in Chapter 3, the WVTR test may underestimate WVTR of porous cellulose sheets due to diffusion of water vapour into the cup being faster than water vapour absorption by the silica gel. For this reason, the WVTR was measured on 50 g m^{-2} cellulose films because the WVTR of a 10 g m^{-2} coating is likely to be too high to be accurately measured using the test.

Figure 5.29 shows the effect of increasing refining, increasing grinding energy, or increasing homogenisation pressure on the WVTR of a 50 g m^{-2} cellulose film. As the CSF decreases, the WVTR decreases significantly from 736 to $226 \text{ g m}^{-2} \text{ day}^{-1}$. The MFC film made from cellulose ground at $3000 \text{ k W h t}^{-1}$ had a WVTR of $82 \text{ g m}^{-2} \text{ day}^{-1}$, indicating another large decrease from the refined pulp sample. This evidence shows that increasing the fibrillation of cellulose from untreated fibres to MFC causes a significant decrease in WVTR of a cellulose film. However, once a threshold level of fibrillation had been reached, further increasing grinding energy did not result in any decrease in WVTR, in fact an overall upward trend in WVTR was seen with increasing grinding energy. Homogenising the MFC causes a slight increase in WVTR. These results suggest that once a dense network of MFC has been reached, further increasing the fibrillation of the cellulose does not result in a decrease in WVTR and may in fact result in a slight increase in WVTR.

Figure 5.20 and 5.22 show that the HVTR is related to FLT index, Curl and Fines B. Since heptane vapour is likely to travel through the cellulose network through gaseous diffusion, the WVTR may be related to the same parameters. Figure 5.30 shows the relationship of FLT, Curl and Fines B with WVTR for refined, ground and homogenised cellulose samples. An initial

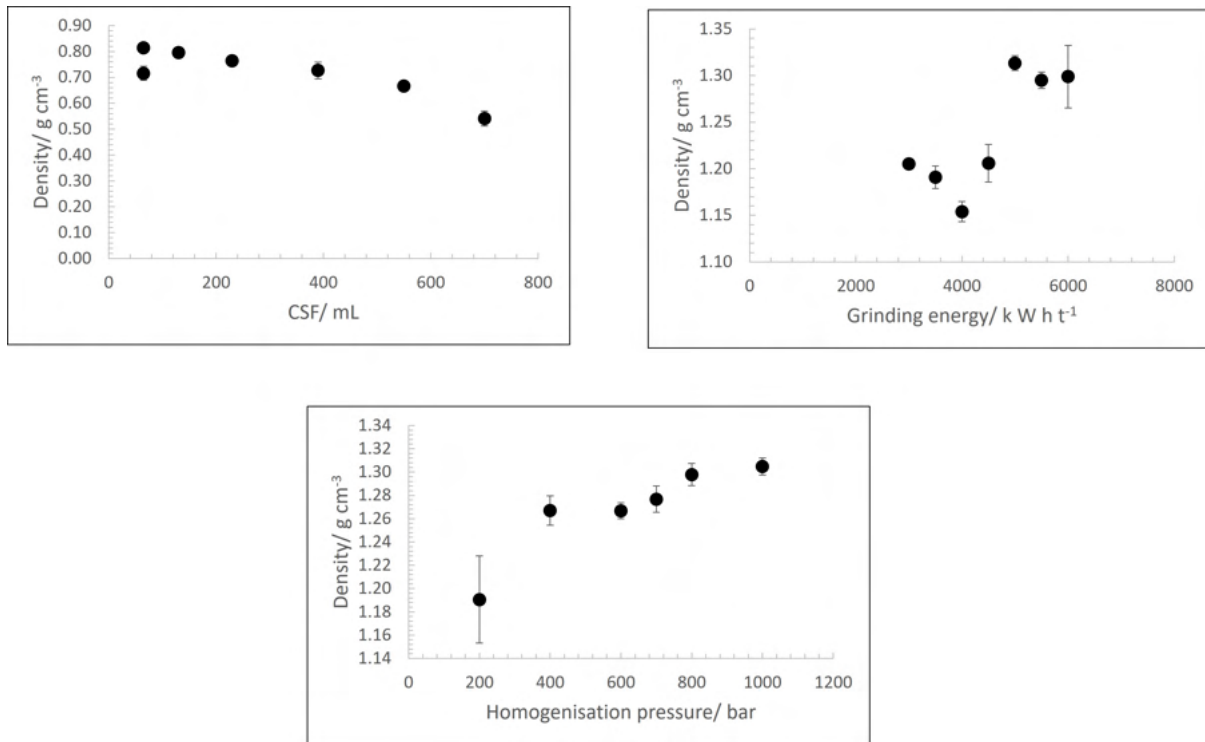


Fig. 5.26. Effect of refining level, grinding energy and homogenisation on the density of cellulose sheets. Density was calculated using thickness measurements from a digital micrometer.

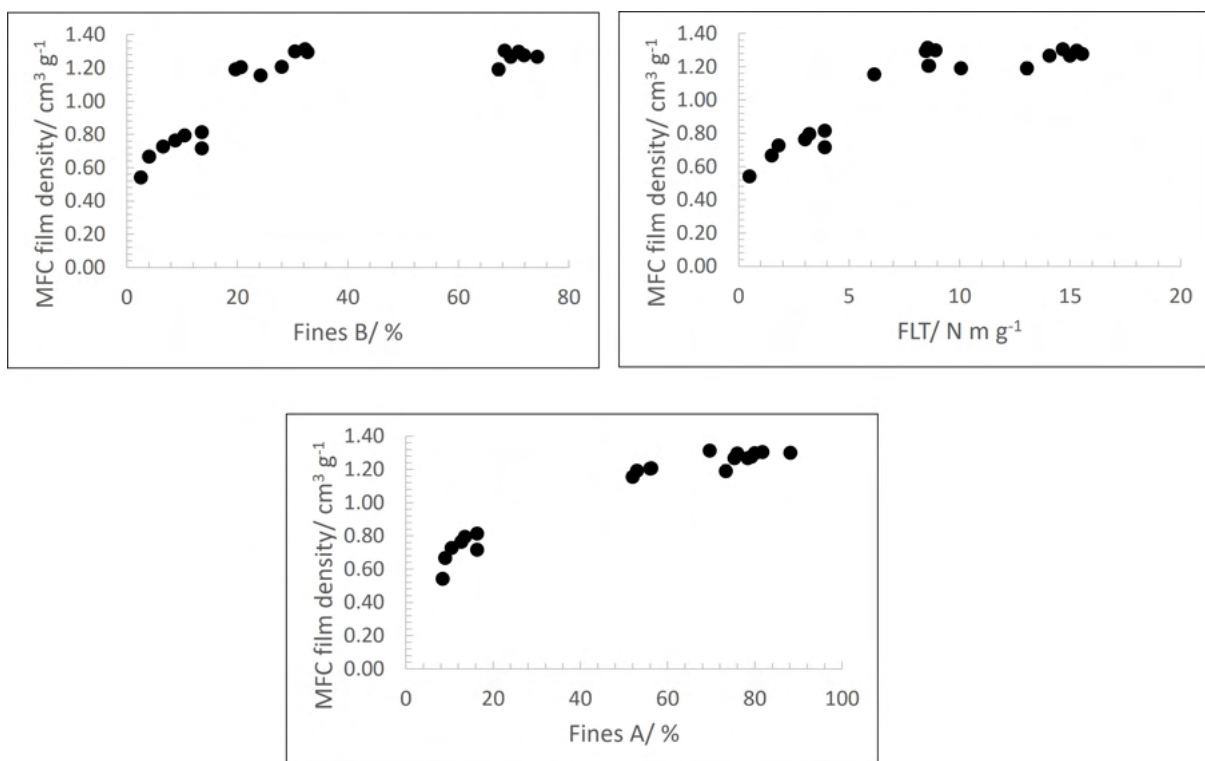


Fig. 5.27. Relation between density of cellulose sheet and FLT index, Fines A, and Fines B of MFC

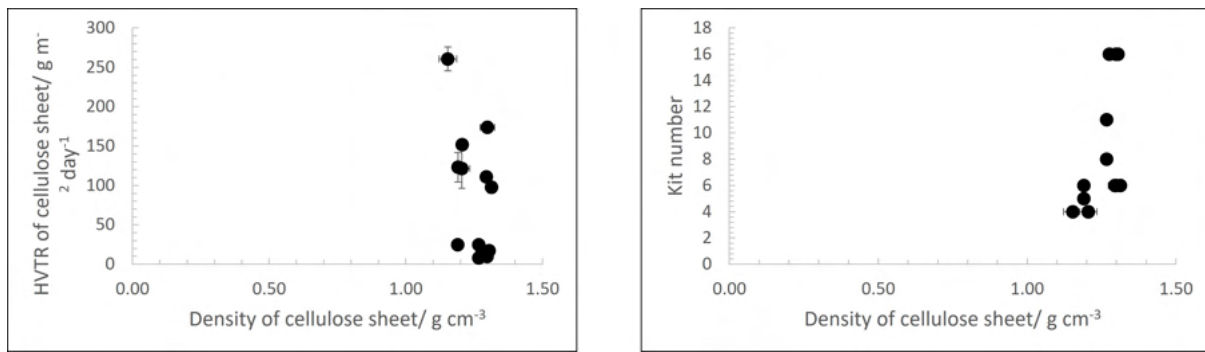


Fig. 5.28. Relation between density of cellulose sheet and HVTR and Kit number of MFC coating.

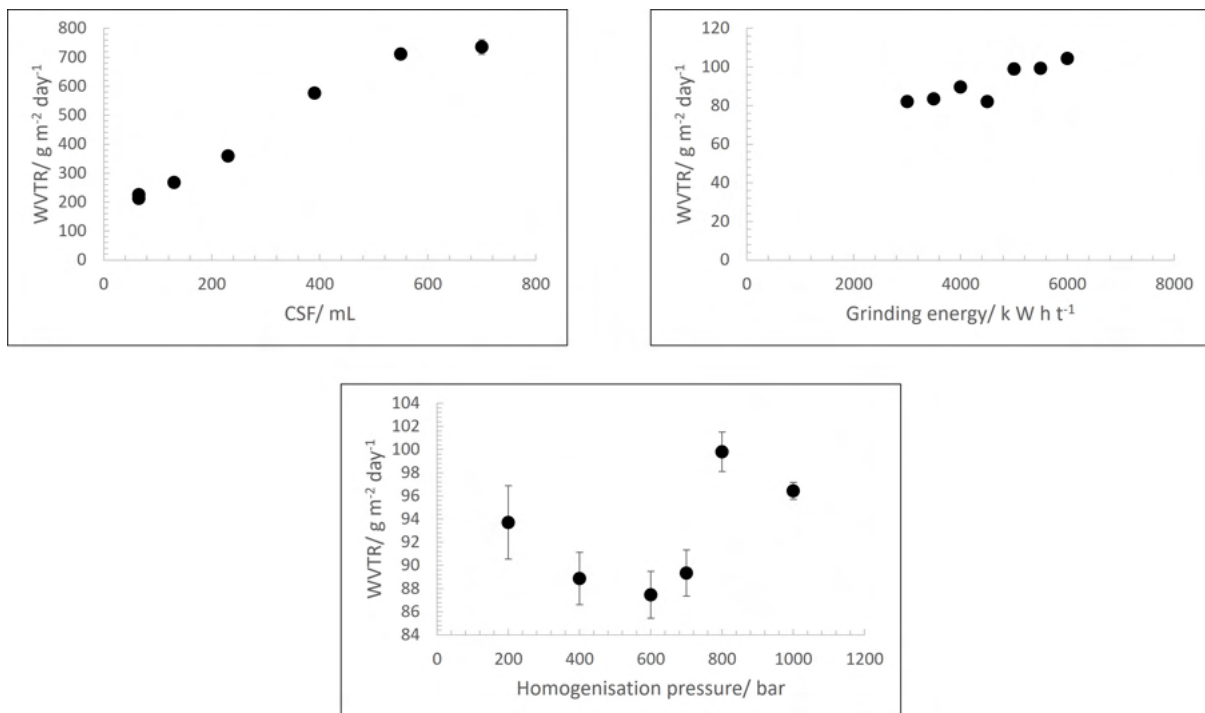


Fig. 5.29. Effect of increasing refining, increasing grinding energy, or increasing homogenisation pressure on the WVTR of a cellulose sheet.

decrease in WVTR is observed for increasing FLT and increasing Fines B as refining increases followed by a plateau. No relationship between WVTR and Curl is observed. Increasing cellulose sheet density corresponds with decreasing WVTR.

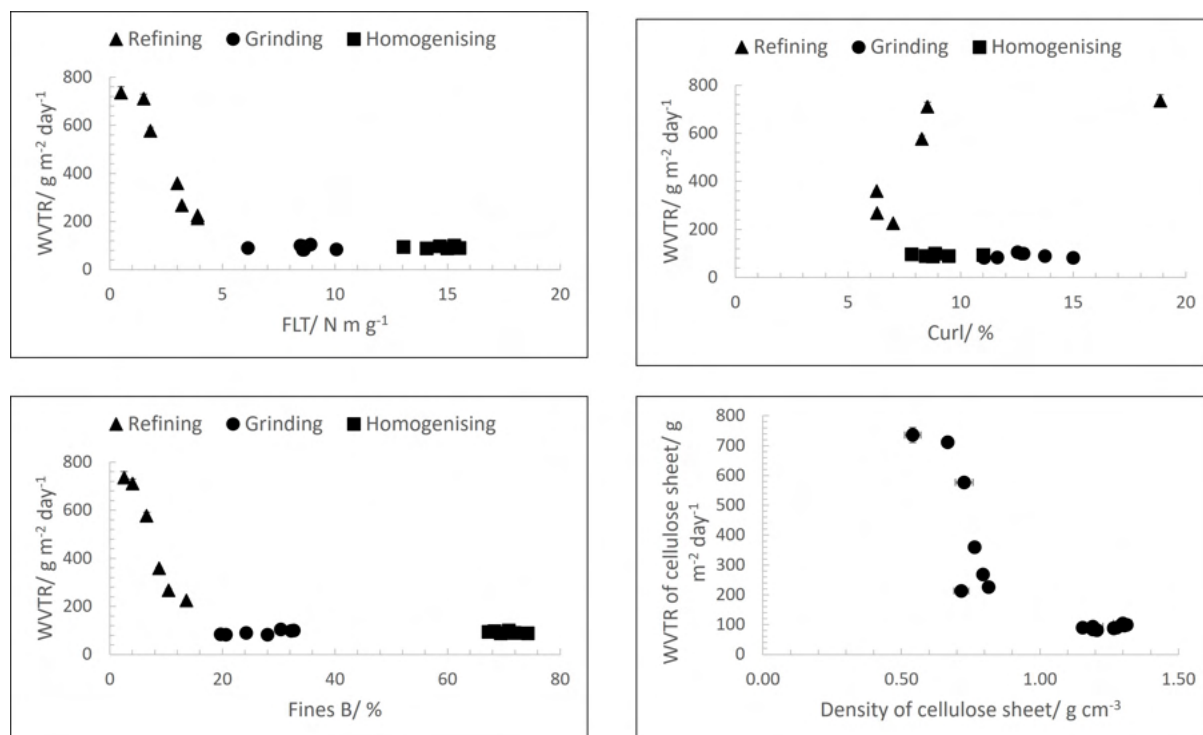


Fig. 5.30. Effect of FLT index, Curl or Fines B on the WVTR of a cellulose sheet.

5.3.11 Light Scattering Properties of Refined Pulp Sheets and MFC Films

Increasing refining of cellulose decreases the opacity of paper due to an increase in density and a corresponding decrease in exposed cellulose surface area.^{135,136} Since MFC can form dense films with little unbonded fibre, the films can have a very low opacity. Nogi and co-authors found that films of MFC were translucent but when the surface was smoothed by sanding, a transparent film was formed, indicating that translucent appearance was due to surface roughness effects.¹⁸² The transparency of an MFC film is thought to increase with increasing fibrillation. Siro and co-authors found a decrease in opacity of MFC films as the numbers of passes through a homogeniser used to fibrillate the MFC increased.⁹¹ Aulin and co-authors also found that increasing number of passes through a homogeniser led to MFC films with a higher transparency.²⁶ Increasing light transmission of MFC films was also observed by Nair and co-authors with increasing number of passes through a Supermasscolloider.⁸⁰

The Kubelka-Munk light scattering coefficient was calculated for the 50 g m⁻² cellulose sheets. The light scattering coefficient at 430 nm is shown as a function of parameters linked to increasing fibrillation of cellulose in Figure- including the FLT index, Fines B, and Fines A in Figure 5.31. It is apparent that increasing the fibrillation initially decreases the light scattering coefficient of cellulose sheets. However, when Fines B, Fines A, or the FLT index further increase— indicating an increasing degree of fibrillation— the scattering coefficient begins to increase.

It was not initially clear why the light scattering coefficient of MFC sheets should begin to increase as the fibrillation of the cellulose increased if the density of the sheets is increasing.

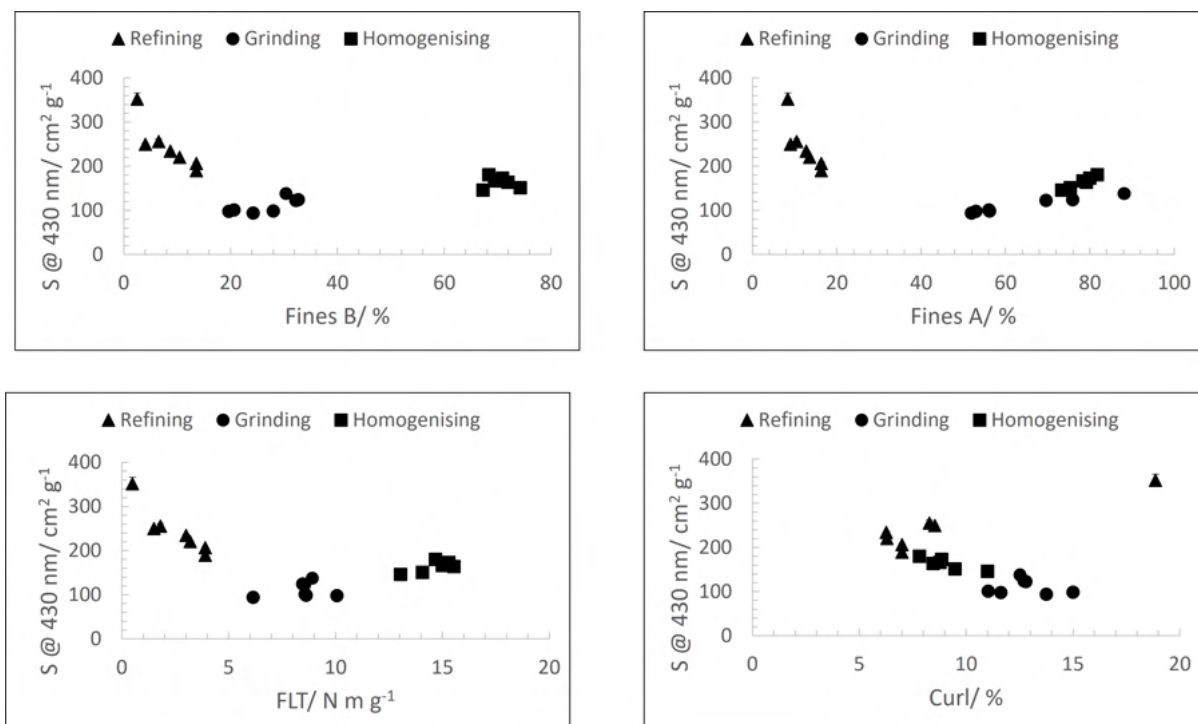


Fig. 5.31. Effect of FLT index, Fines B and Fines A on the Kubelka-Munk light scattering coefficient of cellulose sheets.

However, size of scattering particles strongly influences the wavelength dependence of light scattering, and therefore the scattering coefficient at a particular wavelength.¹³⁷ Gate found that the wavelength dependence on scattering of cellulose membranes was related to the pore size of the membranes and that decreasing pore size lead to a stronger dependence of scattering coefficient on wavelength.¹⁸³ Therefore, the wavelength exponent of the cellulose sheets made in the present study was measured.

The wavelength exponent of the cellulose sheets was calculated from the gradient of a graph of $\text{Log}_{10}S$ as a function of $\text{Log}_{10}\lambda$. This graph produced straight lines for all cellulose sheets. An example is shown in Figure 5.32. The wavelength exponent of the 50 g m^{-2} sheets is related to the FLT index of the MFC, Fines B, Fines A, and Curl in Figure 5.33. Clearly, the wavelength exponent increases with Fines A, Fines B and FLT index, indicating that it increases with increasing degree of fibrillation of cellulose.

The relation between the wavelength exponent of a 50 g m^{-2} MFC sheet is compared to the HVTR and Kit number of 10 g m^{-2} MFC coatings in Figure 5.35. The wavelength exponent does not appear to be related to the HVTR but there is a strong relation with the Kit number. This may be related to the phenomenon of the sharp increase in Kit number as the homogenisation pressure increased. There is also an increase in wavelength exponent as homogenisation pressure increases as shown in Figure 5.34. The increased wavelength exponent with increasing homogenisation pressure implies that the size of the scattering particle is decreasing.¹³⁷ In the case of MFC sheets, the scattering particles are likely to be pores in the cellulose network since only unbonded fibre scatters light. Therefore, Figure 5.34 implies that as the homogenisation pressure increases, the pore size of the cellulose sheets decreases. Figure 5.35 implies that this decreasing pore size may have a significant effect on the Kit number of MFC coated sheets although not a significant effect on HVTR of MFC coated sheets. This may be due to differences in the transport mechanisms of gaseous and liquid oil. Measurement of the wavelength exponent is a simple, rapid process with no need for the

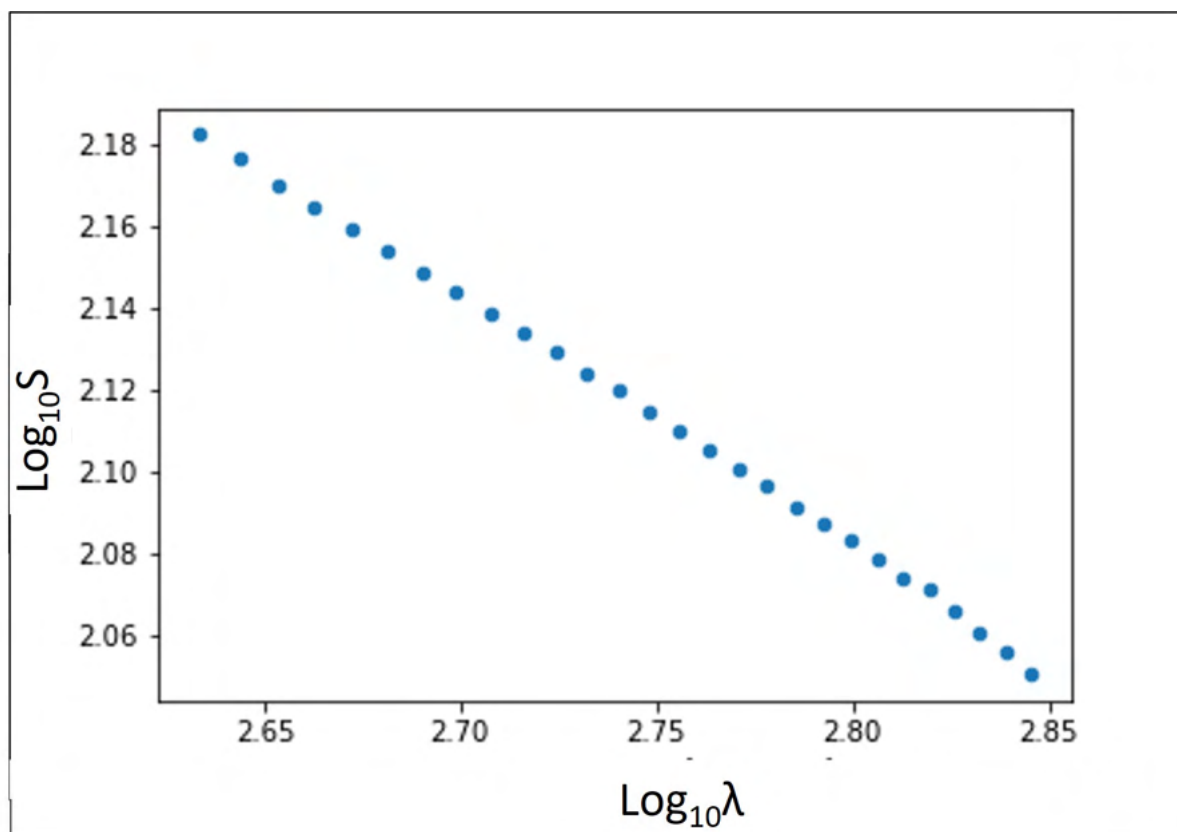


Fig. 5.32. Example of plot of log S as a function of log wavelength for a sheet made from homogenised MFC.

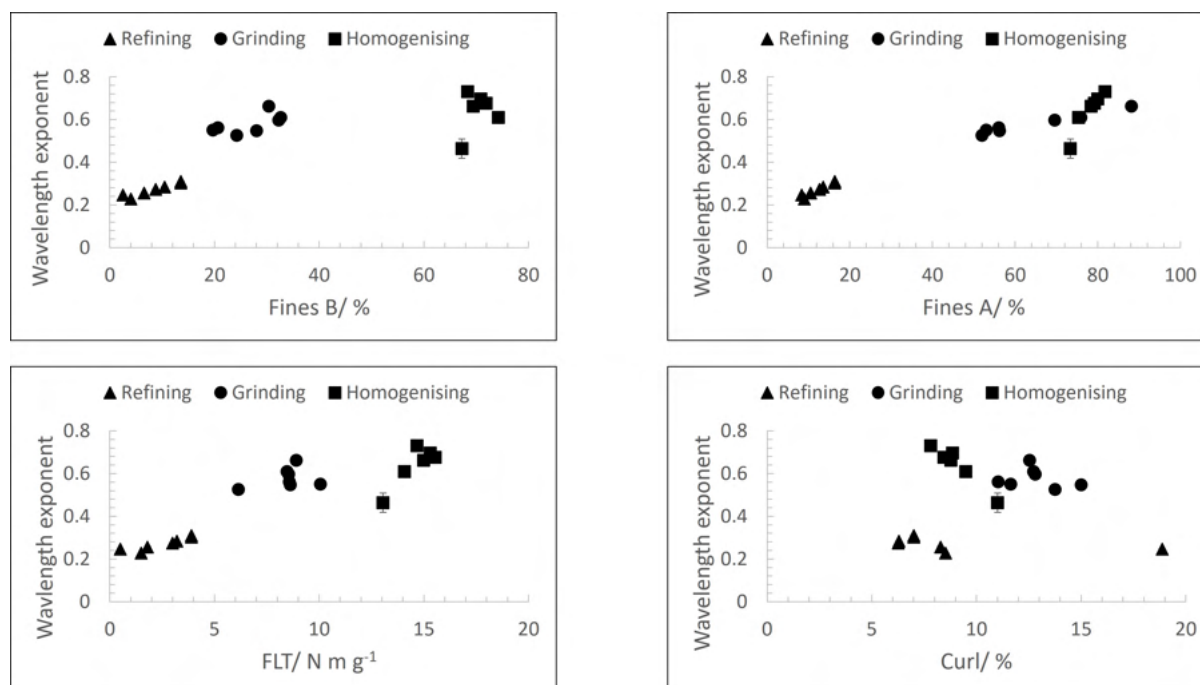


Fig. 5.33. Wavelength exponent of cellulose sheets as a function of FLT index and fibre image analyser parameters Fines B, Fines A and Curl of cellulose samples

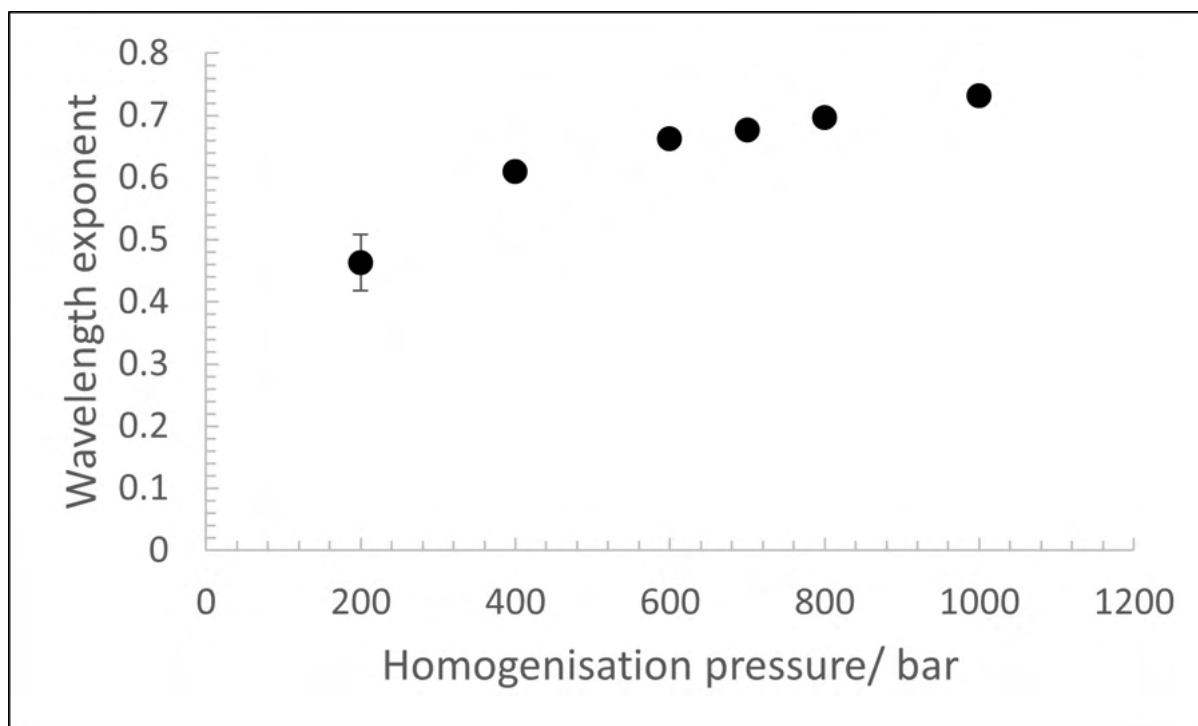


Fig. 5.34. Wavelength exponent of cellulose sheets as a function of increasing homogenisation pressure used to make MFC samples

use of hazardous chemicals. Therefore, if measurements of wavelength exponent could be used as a tool to screen MFC samples for barrier properties, this would be useful as a way to decrease the number of samples that needed to go through the barrier testing stage. Ideally, this process would be done on the cellulose coated sheet rather than separately made cellulose films so that separate samples do not have to be made.

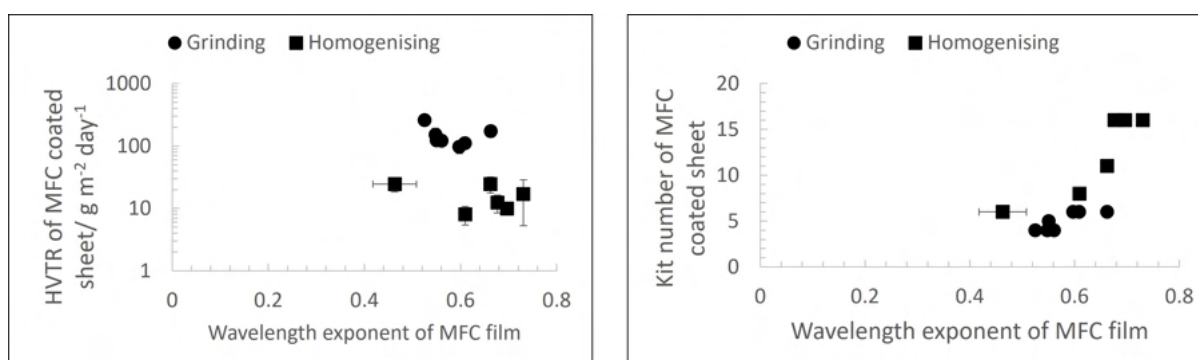


Fig. 5.35. HVTR and Kit number of MFC coatings as a function of wavelength exponent of cellulose sheets

5.3.12 Discussion

Results showed a decrease in air permeability of cellulose coated sheets as refining time increased. Using MFC produced through the Fiberlean grinding process decreased air permeability further. Yook and co-authors found that board coatings of cellulose treated through carboxymethylation prior to grinding in a Supermasscolloider had lower air permeability than board coated with MFC made through mechanical treatment only. The authors suggested this was due to a decreased diameter of the carboxymethylated cellulose fibrils, allowing a more dense network of

cellulose to form.³¹ Similarly, Mousavi and co-workers found that paper coatings consisting of a blend of MFC and CMC had significantly lower air permeability when the MFC was produced through refining followed by a Supermasscolloider grinding stage as opposed to refining only. This was suggested to be because the fine structure of the ground MFC led to formation of a denser coating layer.¹¹⁹

Since heptane is a small, non polar molecule, it can be expected to diffuse through an MFC network in a similar mechanism to oxygen gas. That is, the heptane molecules are likely to diffuse through tortuous connecting pore space in the cellulose network and are slowed by the lack of pore connectivity as suggested for oxygen gas by Aulin and co-workers.²⁶ Therefore, findings from studies looking into the effect of cellulose fibrillation on oxygen barrier properties are relevant to discuss here in relation to the HVTR of MFC coatings. Kumar and co-authors found that an extra fibrillation stage of grinding in a Supermasscolloider did not decrease the OTR of MFC films compared to refining only when accounting for variation in the measurement.⁸⁸ Hasan and co-authors similarly found there was a decrease in OTR of MFC films produced with an additional grinding stage compared to refining only but variation in the OTR measurements meant that this difference was small.²³

The suggestion of Naderi and Lindström that initially increasing fibrillation improves barrier properties but there is a threshold fibrillation level appears to be relevant.⁸⁵ It may be that the MFC samples produced by grinding in this study are still sufficiently coarse that defects exist in the MFC coatings. Once the homogenisation occurs, there is no further measured improvement with increasing homogenisation pressure because there is no more connecting porosity in the MFC film. However, it could also be the case that the limit of the HVTR test has been reached in this case and heptane condensation onto the sheet inside the HVTR pots may be interfering with the results. Potentially, increasing fibrillation of cellulose may be making a difference to the barrier properties but it cannot be measured in the HVTR test.

Therefore, increasing fibrillation of cellulose led to a decrease in air permeability until the detection limit of the instrument was reached and a decrease in HVTR until the level of reliability of the test where heptane condensation begins to interfere with the results. This is likely because the expanded surface area of the cellulose allowed an entangled network of fibrils to form, reinforced through intermolecular bonding, which had decreasing pore space as the fibrils could draw closer together during the drying stage.

Yook and co-authors found that the MFC sample produced using a carboxymethylation pre-treatment prior to grinding in a Supermasscolloider formed board coatings with higher Kit numbers than MFC produced through mechanical treatment only.³¹ Mazhari Mousavi and co-workers found similarly that paper coated with MFC that had undergone an additional grinding treatment after refining had higher Kit numbers than paper coated with MFC produced through refining only.¹¹⁹ Mazhari Mousavi and co-authors also suggest that the mechanism for MFC coatings providing grease resistance to paper is coverage of the pores in the base sheet. In the present study, it may be that the finer cellulose produced through homogenisation was more effective in coverage of pores in the base sheet.

Results of the Kit test appeared to be highly influenced by the presence of small defects-known as pinholes- in the MFC coating. In practicality, this manifested as the Kit solutions passing through into the base sheet in small pinpricks rather than migrating as a larger droplet. This method of failure indicates that as the fibrillation of the MFC increased, fewer of these defects were present. Possibly, the finer cellulose particles could have filled in gaps between larger aggregates or more effectively covered the rough paper surface. Juntunen visualised pinholes on the surface of MFC coatings on filter papers by using a paint brush to apply a solution of Sudan red dye mixed with turpentine and photographing the uncoated side of the filter paper so that the dye solution that had passed through the MFC layer could be easily

seen. Some decrease in the number of pinholes was observed when an MFC with increased fibrillation was applied.⁸²

Therefore, it appears that increasing the fibrillation of the cellulose decreases the volume of connecting porosity within the network, therefore decreasing HVTR and air permeability and increasing grease resistance. Figure 5.36 shows a schematic diagram of how the difference in connecting porosity in the cellulose network is likely to affect the volume of gas that can diffuse through the network. If highly fibrillated MFC contains mostly closed pores or only surface porosity that does not connect throughout the layer, there are fewer pathways for gas diffusion or for grease to be drawn through the network.



Fig. 5.36. Schematic diagram showing how increasing cellulose fibrillation may lead to improved barrier properties due to a lower volume of connecting pore space.

Results showed that increasing FLT index was related to decreasing air permeability, increasing grease resistance and decreasing HVTR of MFC coatings. Lindström suggested that the strength of MFC films depends mostly on the relative bonded area of the film, which can be increased by increasing cellulose fibrillation, also resulting in an increase in density of the film.¹⁸⁴ Naderi and co-authors produced MFC through grafting with CMC and fibrillating with increasing number of passes through a microfluidiser. The study found that both the tensile strength and barrier to oxygen improved as the number of passes increased.⁹² Similarly, Nair and co-workers found that increased fibrillation led to an improvement in both tensile strength and water vapour barrier properties. However, the tensile strength began to show a decrease after further processing which was not seen in the water vapour barrier properties. This was thought to be due to a decreasing fibril length.⁸⁰

Therefore, the present study shows that the FLT test may be an effective way to estimate whether an MFC sample is likely to form effective barrier layers to heptane vapour and grease. This is because increasing the fibrillation of MFC results in a more dense network with a high degree of bonding which can increase the strength of an MFC/mineral composite sheet but can also form an MFC layer with little pore space for diffusing gases and little surface porosity for liquid to wick through when used in an MFC coating with no mineral. Since using an MFC sample with an increasing FLT index decreases HVTR, this suggests that increasing FLT may also lead to a decreased OTR. As the FLT index is a routinely measured quality control parameter in Fiberlean Technologies, this may provide a useful estimation of whether a sample might have good barrier properties when applied as a paper coating.

Results showed that WVTR of cellulose sheets initially decreased with increasing refining energy. Fiberlean MFC sheets had lower WVTR than the laboratory refined pulp sample. However, further increasing the fibrillation did not decrease WVTR. Nair and co-authors also found a plateau in WVTR of MFC films as the fibrillation was increased using increasing numbers of passes through a Supermasscolloider.⁸⁰ It may be that the WVTR does not continue to decrease as fibrillation of the MFC further increases because a dense film of cellulose with no connecting porosity may already have been formed and the measured WVTR could be the rate of water vapour transport through the cellulose network. Okubayashi and Belbekhouche and co-authors suggested that water vapour can diffuse through the amorphous regions of cellulose.^{73,87} Therefore, the plateau in WVTR observed in the present research might be the

measured rate of this form of transport rather than diffusion of water vapour through pores in the sheet.

5.3.13 Conclusions

Improvements in the HVTR and Kit number of MFC coated sheets in the present study indicated there may be a correlation with the FLT index of the MFC which is a Fiberlean quality control measure. This suggests that the FLT index may be a useful parameter to select which MFC samples are likely to have good barrier properties. A slight decrease in crystallinity index was observed for high grinding energy and high homogenisation pressure, but this decrease in crystallinity index appeared to be less important to the barrier properties than the corresponding increase in cellulose fibrillation. Analysis of the light scattering properties of the cellulose sheets suggested that the scattering particle size was decreasing as the homogenisation pressure increased and that this effect was linked to improved grease resistance. Further work in the project aimed to understand whether using a lower energy fibrillation process but increasing the MFC coat weight applied could produce sheets with the same level of barrier properties.

Comparison of the Effects of MFC Type and MFC Coat Weight on Barrier Properties

6.1 Introduction

Chapter 5 showed that increasing the fibrillation of cellulose improved the heptane vapour barrier, grease resistance and air permeability of MFC coated paper. Similarly, increasing fibrillation initially decreased water vapour transmission rate but once a dense cellulose network had been formed, there was no further reduction in WVTR. Chapter 4 showed that increasing MFC coat weight was an effective way to improve the HVTR and grease resistance of MFC coated papers. Therefore, the next stage of the research project was to understand whether an MFC sample with lower fibrillation, likely to be produced with a lower energy demand, could be used in place of a finer MFC sample by increasing the coat weight to compensate for the decrease in barrier properties. An additional benefit of this approach is that increasing the fibrillation of cellulose increases the viscosity and yield stress of MFC suspensions, and therefore using an MFC sample with lower fibrillation may be more suitable for practical, industrial use.⁶⁰ Chapter 5 showed that the FLT index of MFC may be a useful parameter to screen samples for their effectiveness as barrier layers. In the present research, three Fiberlean MFC samples were chosen for analysis with different FLT indices, indicating different levels of fibrillation. A University of Maine MFC sample was also chosen to be used in the study as a reference sample.

6.2 Experimental

6.2.1 MFC Samples

Four bleached kraft pulp MFC samples were used in the present study. Details of the samples are provided in Table 6.1.

Table 6.1
MFC samples used for films and coatings in the present study

Pulp Type	Process Details	FLT index
Eucalyptus	Continuous production, 3500 k W h /t	10.7
NBSK	Supermill, 4000 k W h/t grind, 700 bar homogenised.	15.5
Acacia	Supermill, 3000 k W h t, continuous production	6.2
University of Maine MFC	Refiner product	11.6

6.2.2 MFC Characterisation

The following methods were used to characterise the MFC samples used in this study:

- Valmet fibre image analyser
- DIC optical microscopy
- Viscosity as a function of shear rate at 1% MFC solids content
- Yield stress of MFC suspensions at 1% solids content
- SEM analysis (excluding the acacia material)

6.2.3 MFC Coatings and Films

MFC was coated using vacuum filtration onto a Suzano commercial base paper using the method described in Chapter 4. The initial purpose of the study was to compare the acacia MFC with the NBSK MFC, since Chapter 5 showed that the extent of fibrillation of MFC, measured by increasing FLT index, was important in determining how effective an MFC coating would be as a barrier. Therefore, the acacia and NBSK MFC were coated at 3, 6, and 9 g m⁻². For the acacia MFC, it was expected that the coatings may be less effective barrier layers so an additional coat weight of 12 g m⁻² was also applied. The eucalyptus and University of Maine MFC samples were then used as reference samples and applied at 6 and 9 g m⁻².

The following tests were performed on MFC coated sheets

- Bendtsen porosity
- HVTR
- Kit testing
- Laser interferometric profilometry

MFC films were made through vacuum filtration at 50 g m⁻² according to the method described in the Experimental chapter. The following tests were performed on MFC films

- Optical microscopy
- Laser interferometric profilometry
- SEM imaging (surface and cross section)
- Optical properties
- Density (through measurements of thickness made with a digital micrometer)
- WVTR
- HVTR
- Mercury porosimetry
- Nitrogen pycnometry

6.3 Results

6.3.1 MFC Characterisation

Fibre Analyser Properties

Figure 6.1 shows the percentage of the length weighted distribution of fibre fragments with a width above 10 μm in the four MFC samples. The acacia MFC sample clearly contains the highest percentage of fibre fragments between 0-0.2 mm in length. The NBSK sample appears to show the highest percentage of long fibre fragments.

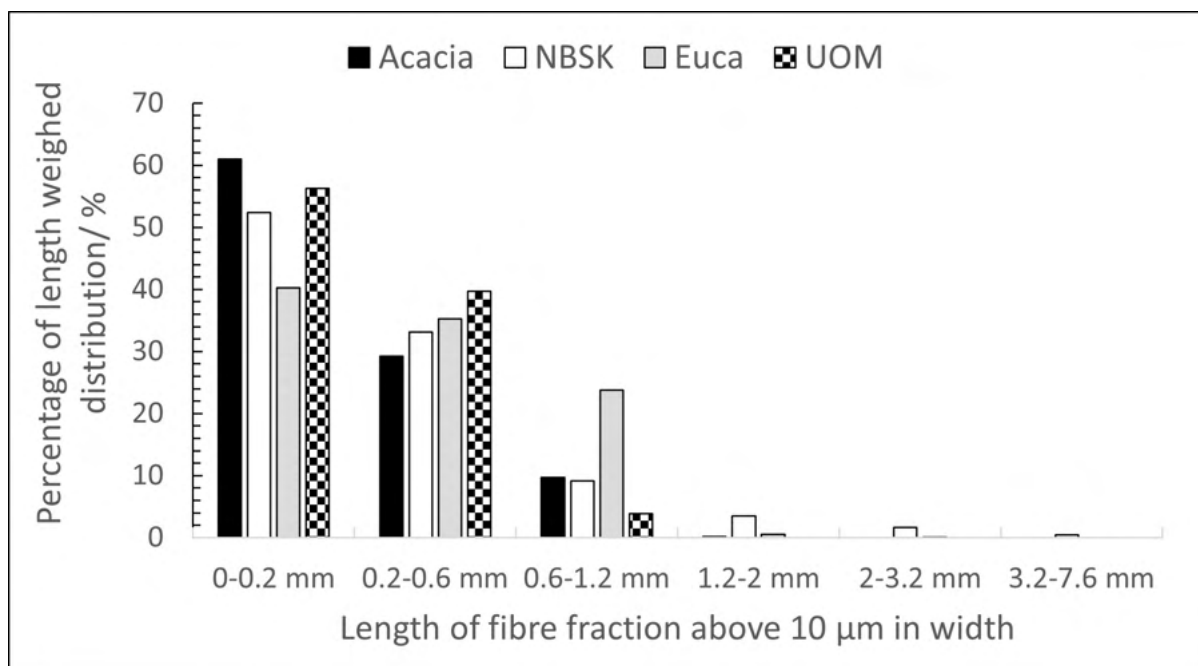


Fig. 6.1. Percentage of length weighted distribution of large fibre fragments measured through Valmet fibre image analyser. UOM refers to the University of Maine MFC sample.

Figure 6.2 shows the relationship between Fines A and Fines B for the MFC samples used in the current study. It is apparent that the NBSK and University of Maine MFC samples have significantly higher Fines B than the acacia and eucalyptus samples.

Optical Microscope Imaging of MFC Samples

Figure 6.3 shows optical microscope images of the four MFC samples used in coating. The eucalyptus sample appears to contain short fibre fragments along with extensive aggregated fibril structures. The acacia sample contained more coarse fibre residues along with some short fibril aggregates. The NBSK and University of Maine samples both contained some large fibres but also networks of fine cellulose fibrils. The microscope images show some discrepancies with the fibre image analyser data. For example, Figure 6.1 shows that the NBSK MFC had the highest proportion of long fibre fragments. However, the fibre image analyser takes the analysis from 2000 images, whereas only 20 images per sample were taken for optical microscopy.¹²³ Therefore, although a representative image out of the 20 was chosen for each MFC sample, there will clearly be less representation than can be provided by the fibre image analyser.

Rheology of MFC Samples

Figure 6.4 shows the increase in shear viscosity of MFC suspensions at 1.0% solids as the shear rate increased. The acacia MFC suspension showed the lowest overall viscosity, followed by

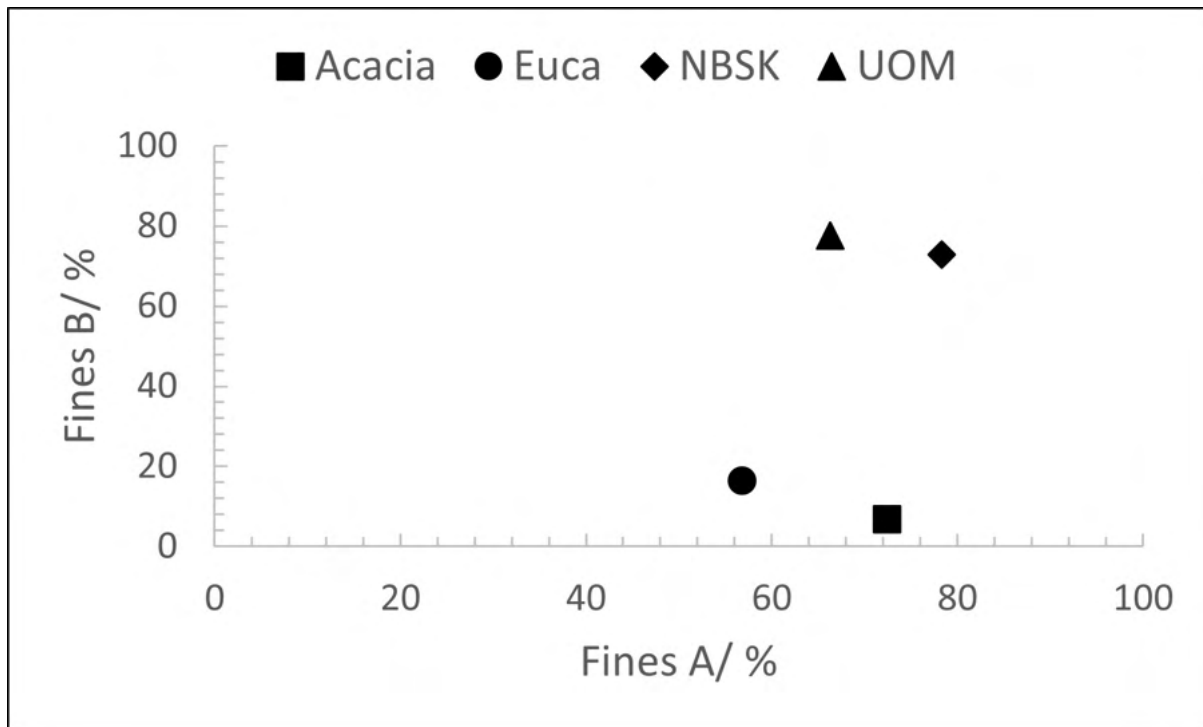


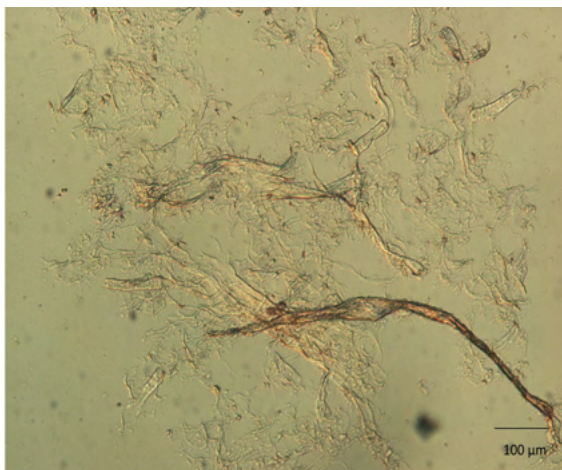
Fig. 6.2. Fines A and Fines B of MFC samples measured through Valmet fibre image analyser. UOM refers to the University of Maine MFC sample.

Table 6.2

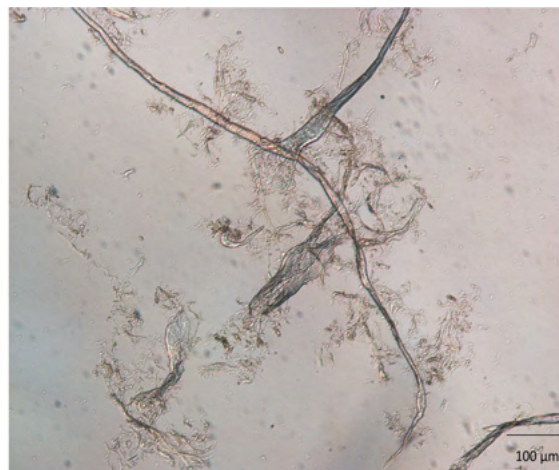
Yield stress of 1.0% solids MFC suspensions measured through an oscillation amplitude sweep with a roughened cup and bob geometry.

MFC sample	Yield stress/ Pa	Standard deviation/ Pa
NBSK	4.89	1.56
UOM	3.66	0.21
Acacia	0.42	0.02
Eucalyptus	2.33	0.17

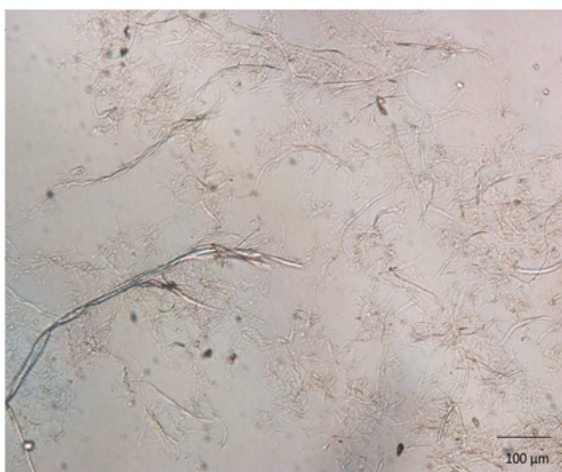
the eucalyptus MFC suspension. The NBSK and University of Maine MFC suspensions shows similar viscosity. Figure 6.5 shows data from the oscillation amplitude sweeps on the MFC suspensions. Table 6.2 shows the yield stress of the MFC suspensions, which is here is defined as the complex shear stress at a 45° phase angle. The NBSK MFC suspension had the highest yield stress, followed by the University of Maine sample. The eucalyptus MFC suspension had a lower yield stress than the NBSK and University of Maine samples but the acacia MFC had a yield stress an order of magnitude lower than the other samples. Looking at Figure 6.3, the acacia MFC sample appears to be comprised of some large fibre fragments and many short fibrils. Cinar Ciftci and co-authors found that increasing aspect ratio of MFC suspensions led to higher measured values of yield stress (Supplementary Information).¹⁸⁵ However, in this case, the authors created suspensions of MFC with different aspect ratios through separating an MFC suspension into various size fractions rather than comparing samples produced from different pulp types and process conditions.



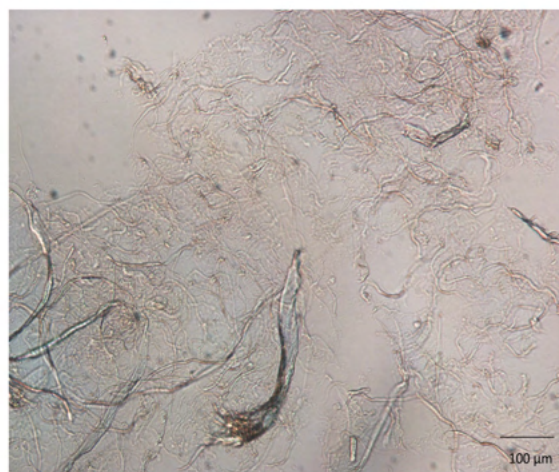
Eucalyptus



Acacia



NBSK



University of Maine

Fig. 6.3. DIC optical microscope pictures of 0.08 wt% MFC suspensions.

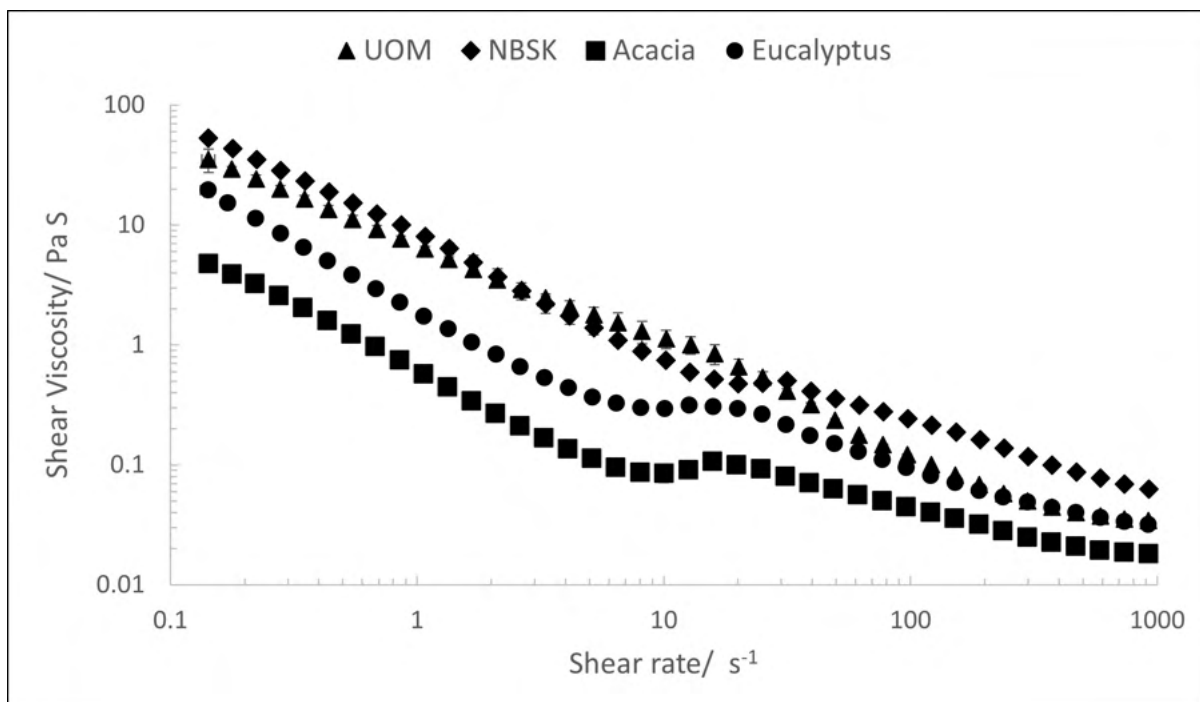


Fig. 6.4. Shear rate ramp up for MFC suspensions at 1.0% solids using a roughened cup and bob geometry. Shear rate was increased logarithmically and both shear viscosity and shear rate are presented on a logarithmic scale. Data shows an average viscosity from three tests per geometry and error bars represent standard deviation.

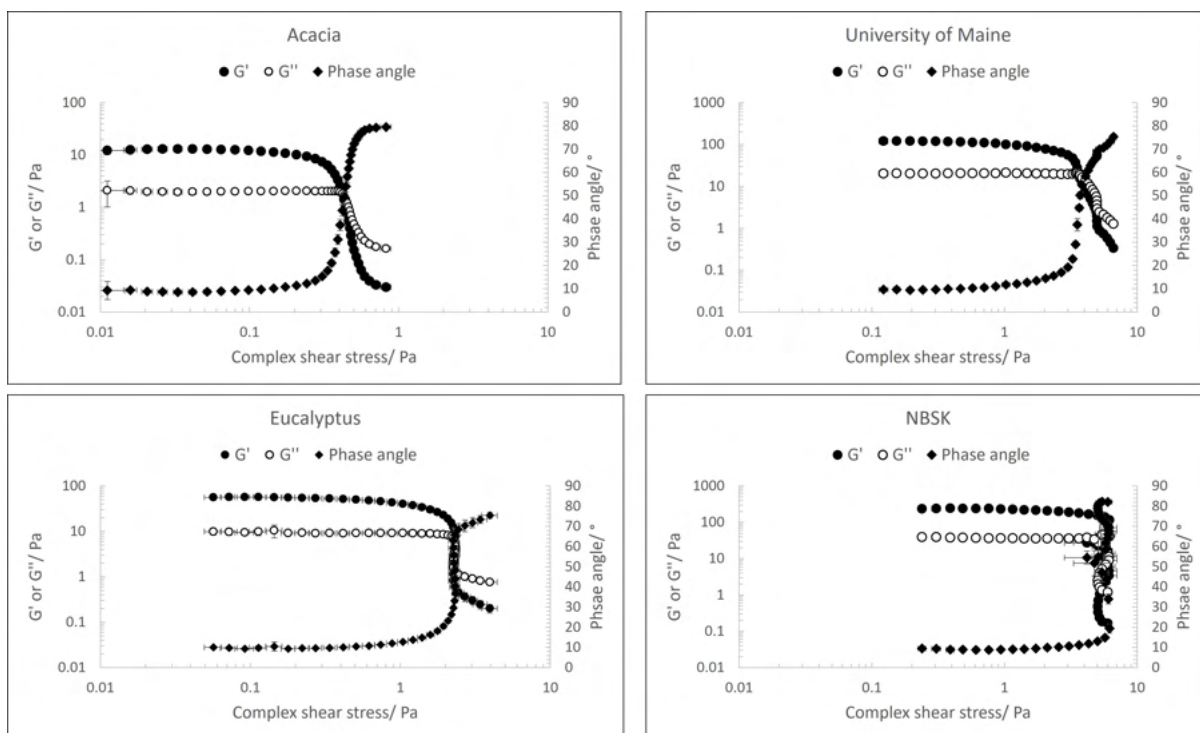


Fig. 6.5. Amplitude sweeps for MFC suspensions at 1.0% solids using a roughened cup and bob geometry. Shear modulus and complex shear stress are presented on a logarithmic scale. Data shows an average viscosity from three tests per geometry and error bars represent standard deviation.

6.3.2 MFC Films

Optical Microscopy of MFC Films

To study the differences in barrier coating properties of the four MFC samples, films of MFC were made through vacuum filtration at 50 g m^{-2} . Optical microscope images of the films are shown in Figure 6.6. Large fibre fragments are visible in the NBSK MFC film. The eucalyptus and acacia MFC films also contain many fibre fragments, although they are smaller than the NBSK fibres, which is most likely related to the different pulp types. There are no larger fibres visible in the University of Maine MFC film. Micrographs of the MFC films are consistent with the fibre image analyser data in Figure 6.1, since the large fibre fragments are visible in the film made from NBSK MFC, and are seen as a higher percentage of fibres above 1.2 mm in Figure 6.1. This may be because the mass of cellulose being visualised in the optical microscope image is larger, therefore a more representative image can be captured. 9 images were captured across two separate films for each MFC sample and a representative image was selected for each MFC sample.

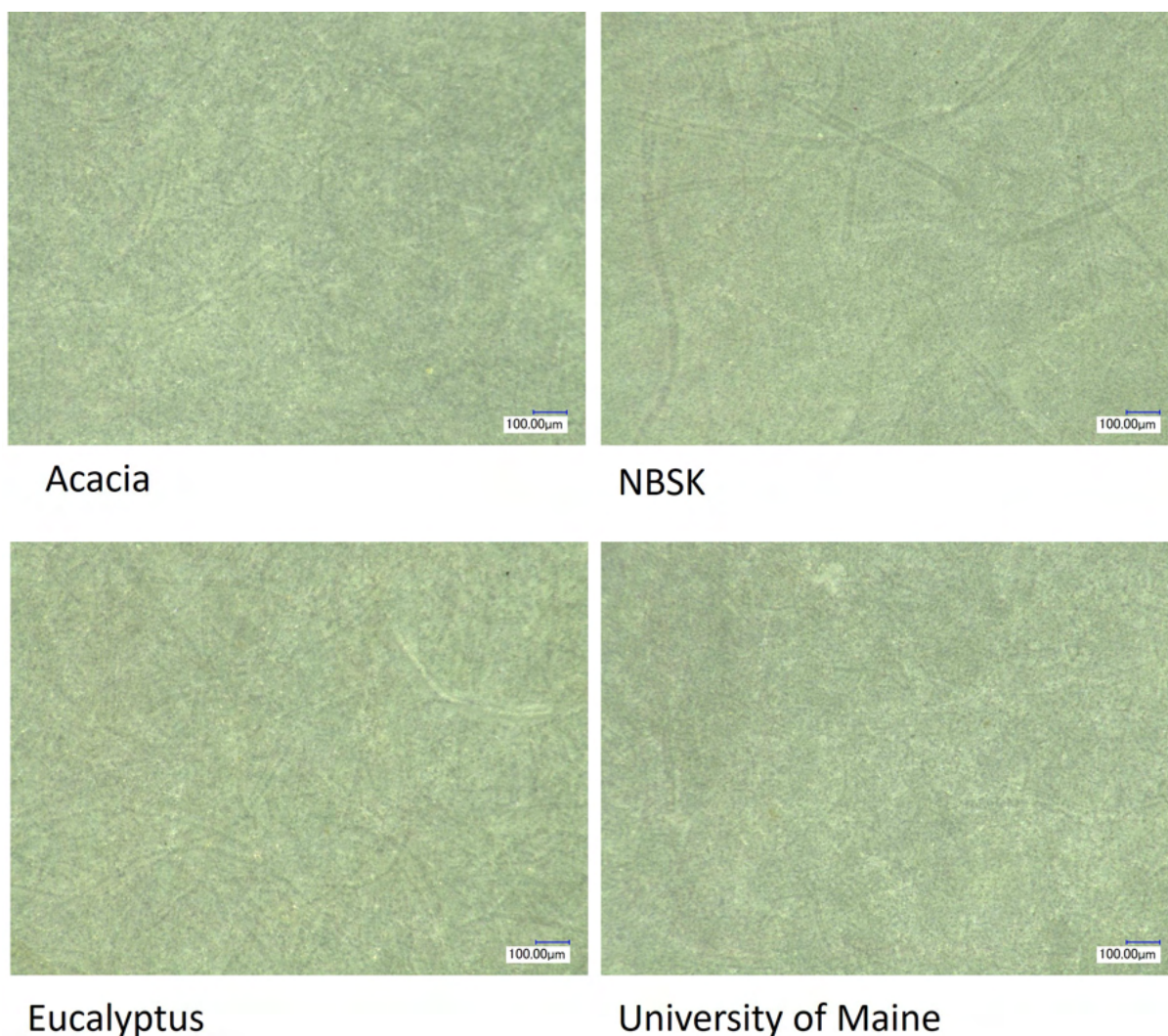


Fig. 6.6. Optical microscope images of MFC films visualised using a Keyence microscope.

Laser Surface Profile of MFC Films

Figure 6.7 shows laser height profile images of the MFC films samples. The NBSK film samples clearly shows a height disturbance caused by a large fibre. The presence of fibre fragments causing a disturbance in the film structure is also seen in the eucalyptus MFC film. Two images were captured for each MFC sample. If more images had been available, a quantitative analysis of the height disturbances could have been attempted. However, it requires two hours to produce one image using the laser interferometric profilometer, therefore making it impractical to collect enough representative images for this analysis. Comparing these images to optical microscope images in Figure 6.6, it is clear that the height profiles of large fibres are consistent with representative optical micrographs of the films.

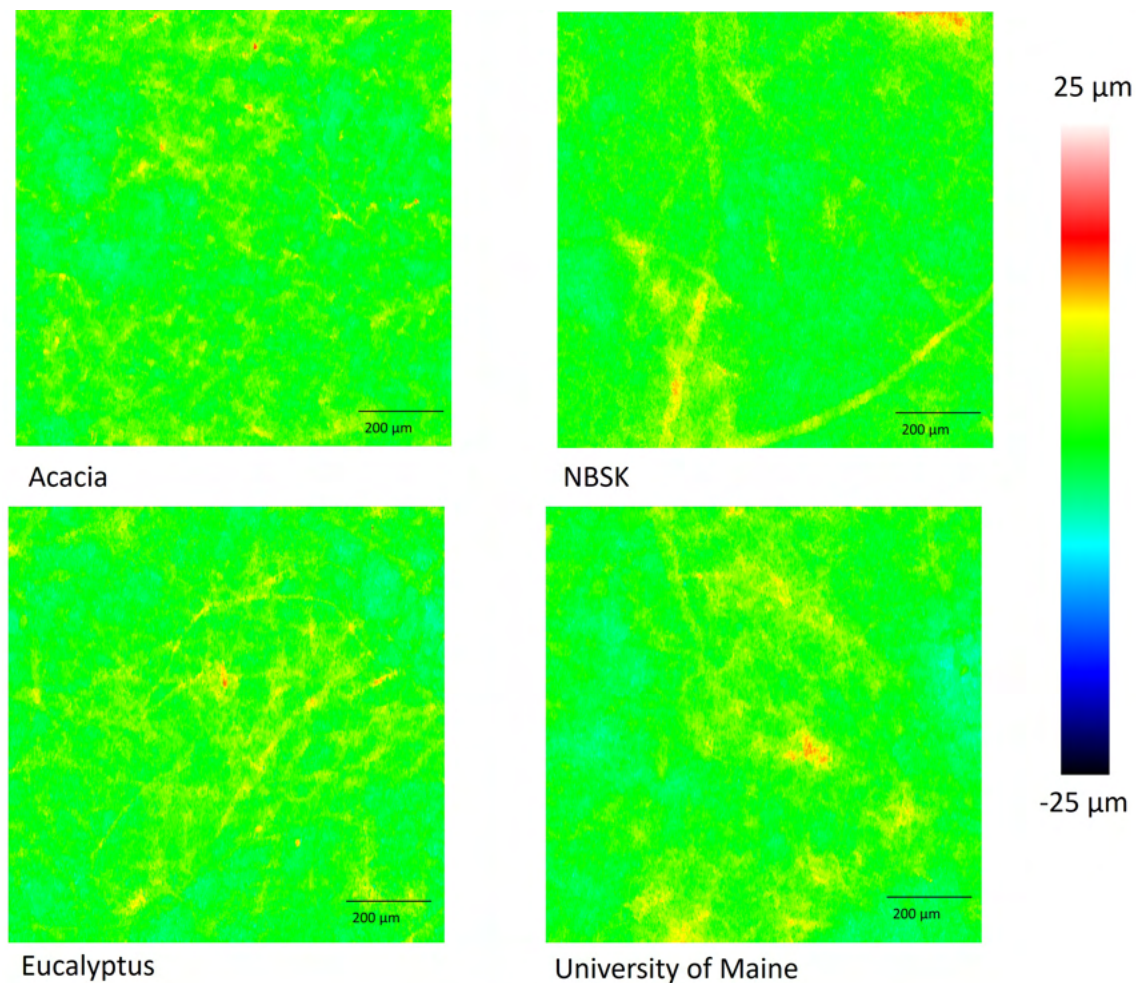


Fig. 6.7. Laser height profiles of MFC films measured using an interferometric laser profilometer.

SEM Images of Film Surface and Cross Sections

To further understand the structure of the MFC films, SEM images of surface and cross sections of the films were provided by IMERYS Microscopy department. The surface and cross section of the MFC films are shown in Figure 6.8 to Figure 6.11. The acacia MFC film surface viewed in low magnification appears disturbed by a fibre fragment which creates porosity in the surface of the layer. At higher magnification, some porosity is visible in the surface of the film. At lower magnification, the presence of large fibres is apparent in the NBSK MFC film. However, the fibres appear to be embedded into the film rather than disturbing the

surface in contrast to the acacia MFC films. At higher magnification, the surface of the NBSK film shows less porosity than the acacia MFC film. Cross sections of the films show a dense structure although there appears to be some cracks in the films. This could be part of the true structure of the film but may also be cracks that formed when the cross sections of the MFC film were cut.

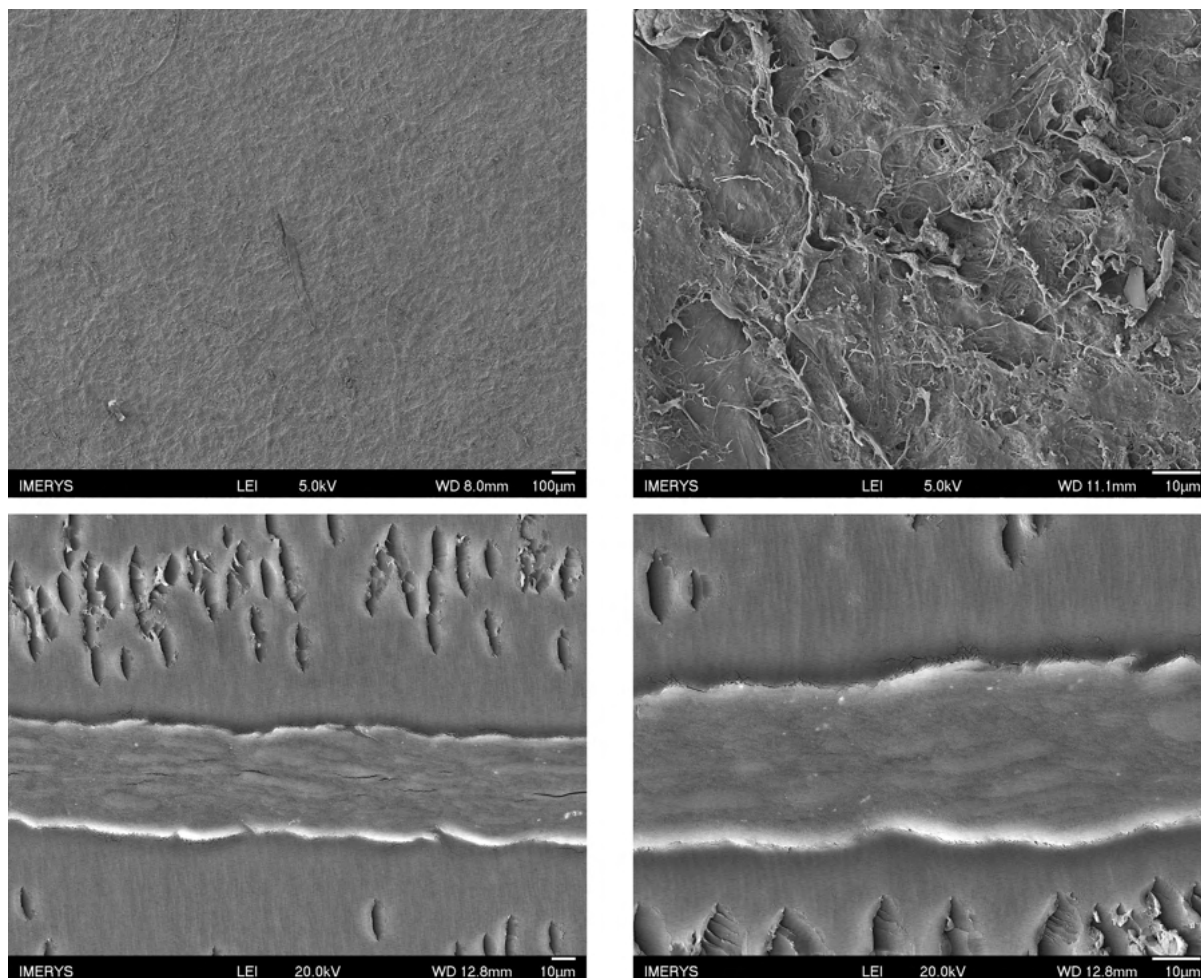


Fig. 6.8. SEM images of acacia MFC films. Top row is the surface of the films and the bottom row is cross sections of the films.

Density of MFC Films

Figure 6.12 shows the density of MFC films measured using a digital micrometer. The University of Maine and NBSK MFC films had the highest density with the eucalyptus MFC film showing the lowest density.

To further study differences in density between the eucalyptus MFC film and the NBSK MFC film, nitrogen pycnometry was performed to calculate the volume of chamber filled with an MFC film with a known mass. The results are shown in Figure 6.13. This measurement intended to provide the skeletal density of the films, which is the density of the solid phase of material. Generally, the measurement is performed with helium gas, and it is assumed that helium is able to penetrate into the material and fill closed pores.^{186,187} However, in this case the measurement was performed with nitrogen gas. Fukuzumi and co-authors found that the permeability of nitrogen gas in an MFC film was lower than oxygen and close to the detection limit of the instrument, indicating very low gas permeability.¹⁸⁸ Roilo and co-workers found that the permeability of Helium gas in an MFC film was significantly greater than nitrogen.⁷⁰

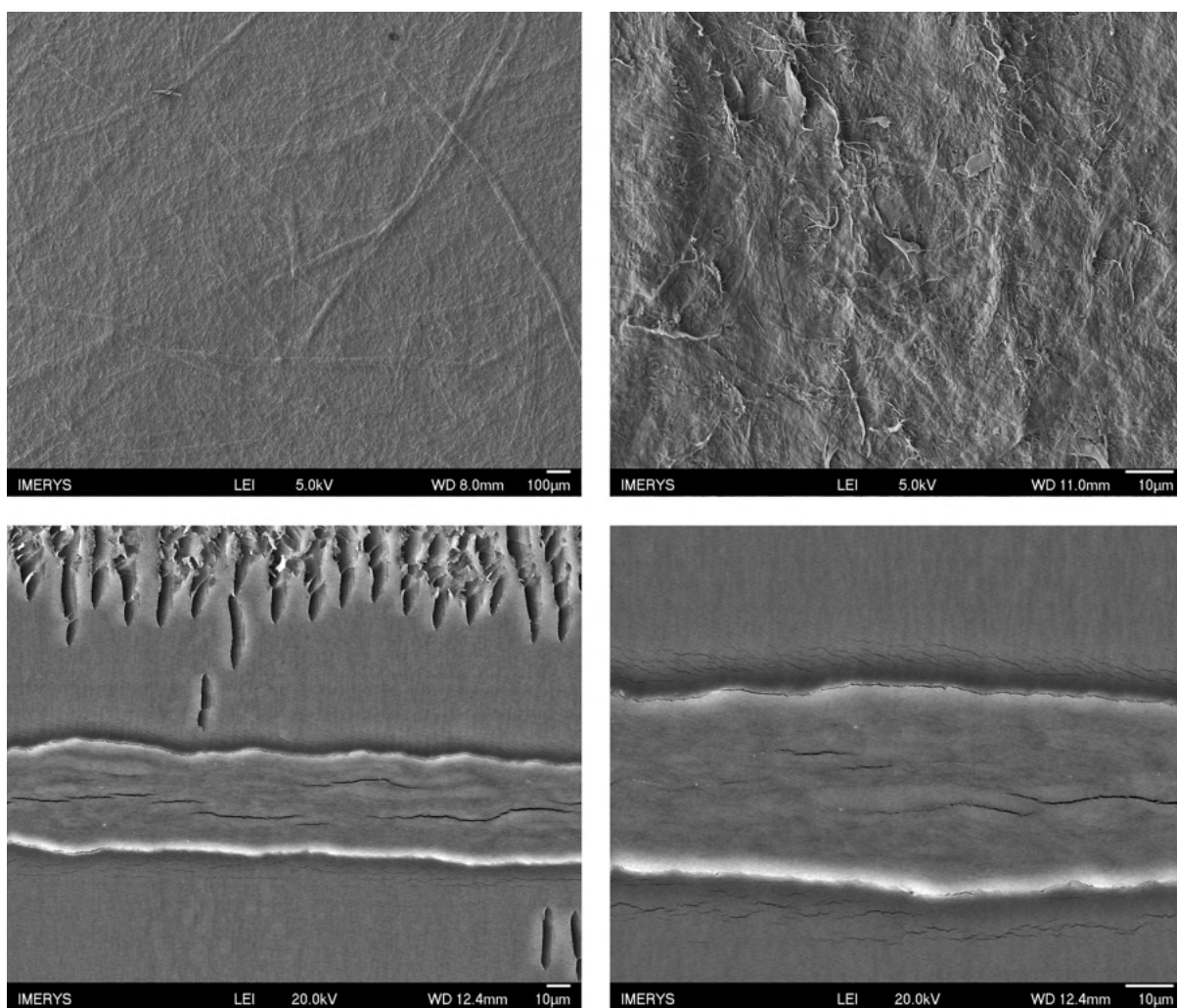


Fig. 6.9. SEM images of NBSK MFC films Top row is the surface of the films and the bottom row is cross sections of the films.

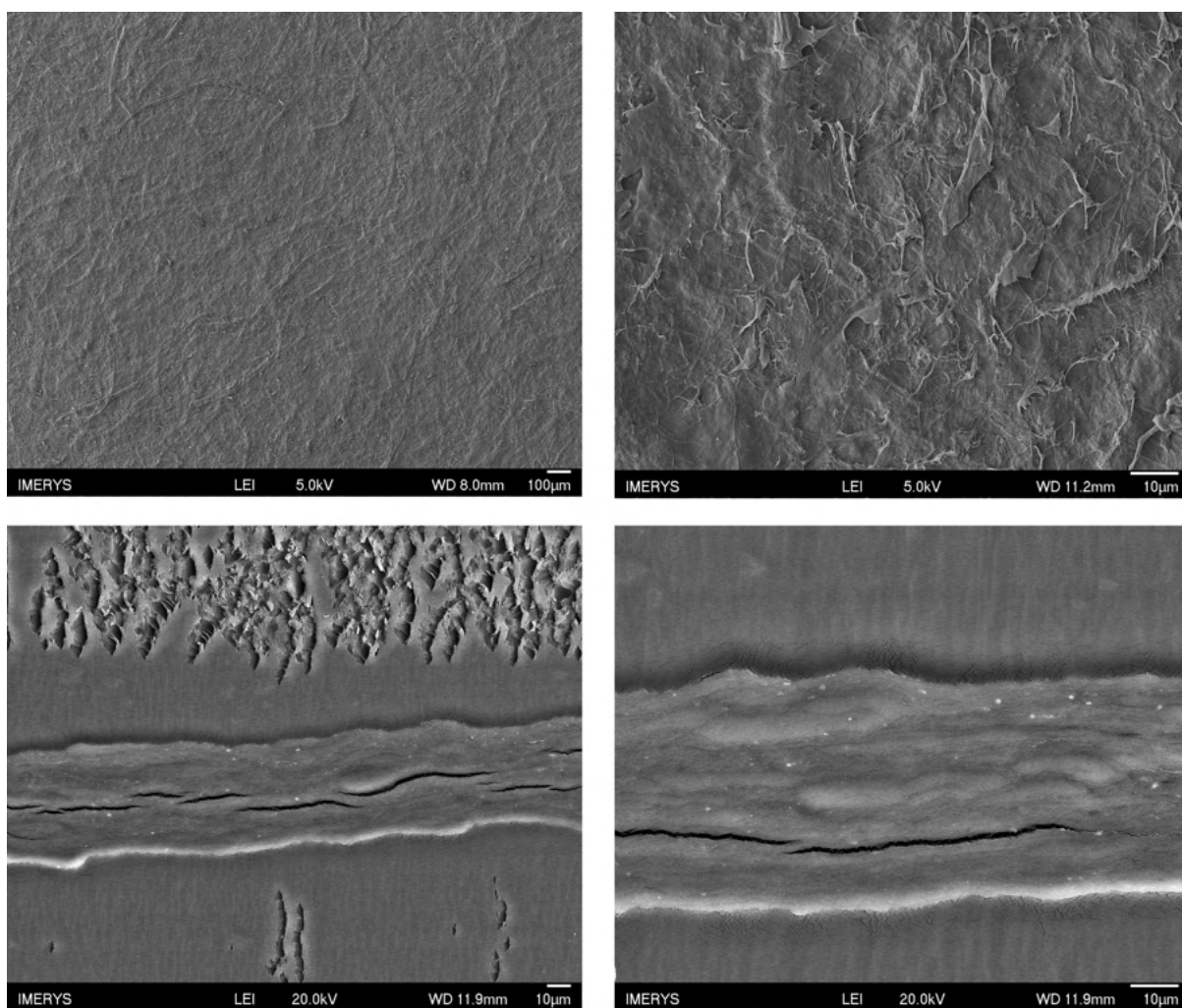


Fig. 6.10. SEM images of eucalyptus MFC films Top row is the surface of the films and the bottom row is cross sections of the films.

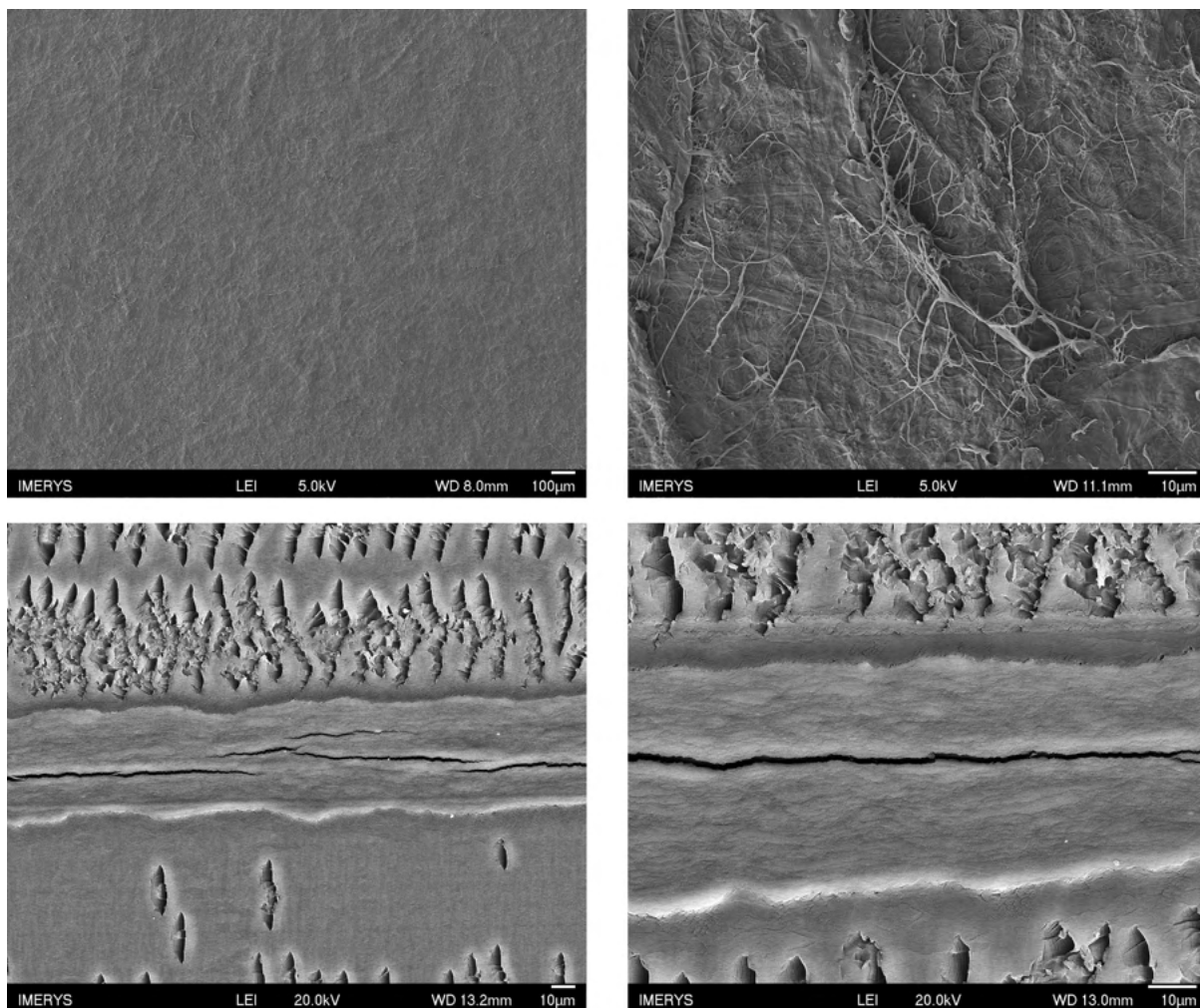


Fig. 6.11. SEM images of University of Maine MFC films Top row is the surface of the films and the bottom row is cross sections of the films.

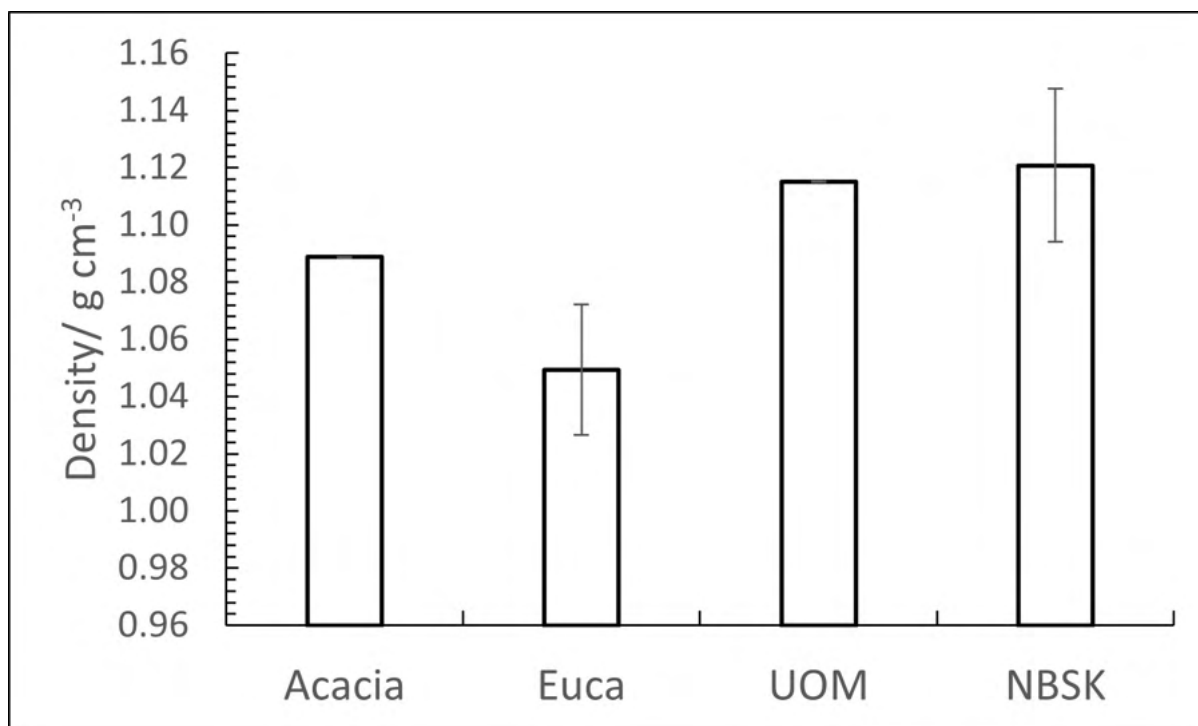


Fig. 6.12. Density of MFC films measured at 50% RH using the mass per area of the film and the thickness measured using a digital micrometer.

Therefore, pycnometry of MFC films with nitrogen gas in place of helium gas is likely to mean that the penetration of gas into closed pores of the materials may take longer as the rate of transmission is likely to be slower.

Figure 6.13 shows that the density of the films was between 1.607 and 1.574 g cm^{-3} . The density of crystalline cellulose was measured as 1.676 g cm^{-3} by Diddens and co-authors.^{26,189} Mazeau and co-authors calculated the density of amorphous cellulose to be between 1.34 and 1.39 g cm^{-3} .¹⁹⁰ The density measured through pycnometry is therefore between that of crystalline and amorphous cellulose which suggests that the skeletal density is being accurately measured.

Density measurements performed using the digital micrometer were in the range of 1.05 - 1.12 g cm^{-3} . This is lower than that suggested from the pycnometer measurements. The pycnometer measurement describes the skeletal density of the cellulose, whereas the micrometer measurement describes the thickness of the film, inclusive of air voids, which is why the calculated density is lower. However, it is not possible to directly compare the two measurements to calculate the pore volume because the measurement conditions are different. The micrometer measurements were performed in a 50% RH environment so some water had adsorbed into the cellulose structure. Additionally, use of a micrometer to measure the thickness of MFC films may result in an overestimate due to surface roughness in the film caused partly by larger fibre fragments. This may lead to an under-estimation of film density. However, the advantage of the micrometer measurements is that many repetitions can be quickly and simply measured.^{191,192}

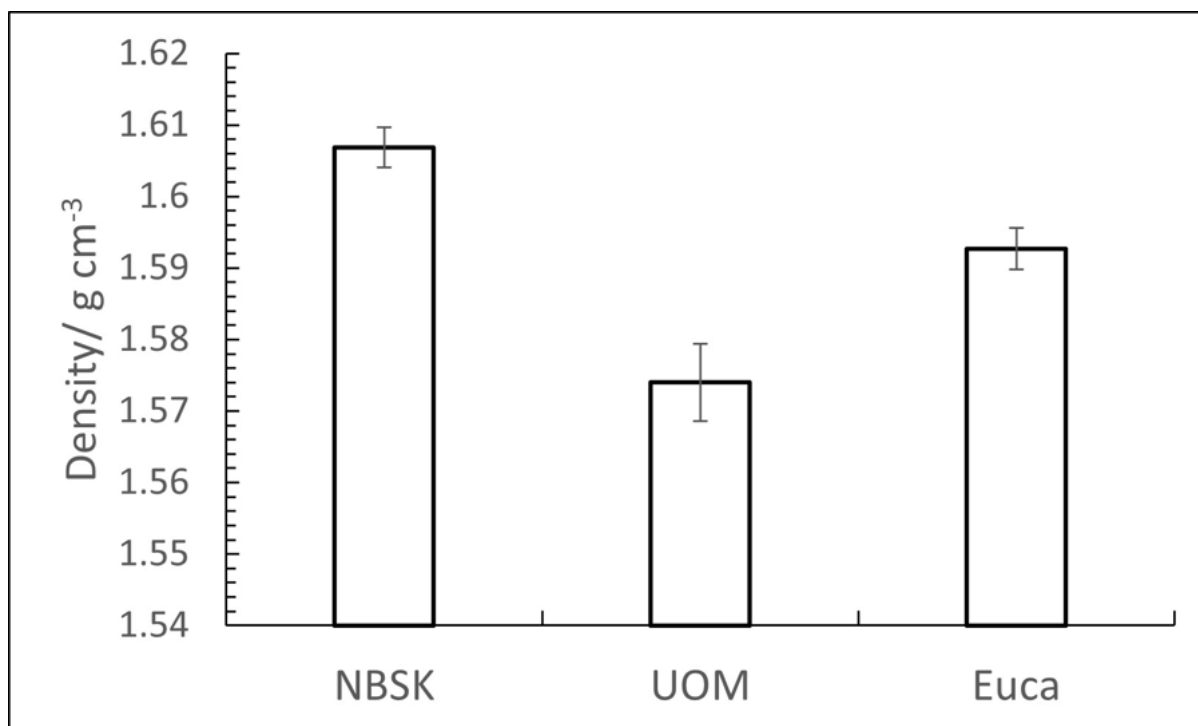


Fig. 6.13. Density of MFC films measured using a Nitrogen pycnometer. Error bars represent standard deviation from 10 chamber filling and de-gassing runs.

Density can also be calculated through mercury porosimetry data. However, Figure 6.14 shows that the mercury porosimetry data for MFC films showed significant noise at pore sizes above 10 μm . Therefore, the calculation of density may not be accurate. The films show some porosity between 0.05 and 0.01 μm . The fitting parameters for the porosimetry data were adjusted to include only the data below 10 μm so that the differences in fine pore structure within the films could be evaluated. This is shown in Figure 6.15. All MFC samples show pores are present in the diameter range of 0.1- 0.01 μm .

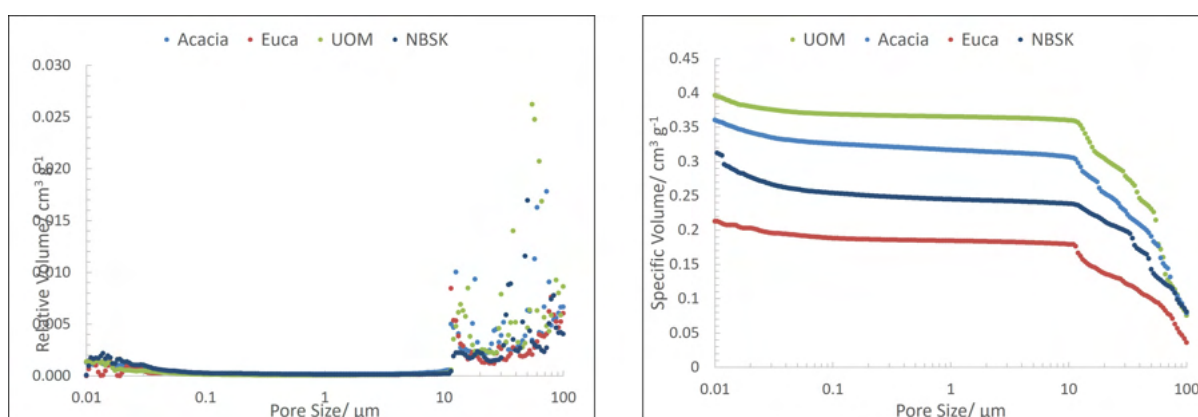


Fig. 6.14. Mercury porosimetry analysis of MFC films

Light Scattering Properties of MFC Films

Figure 6.16 shows that the University of Maine MFC film showed the lowest light scattering coefficient at 430 nm. The wavelength exponent of the eucalyptus MFC film was highest out of all samples.

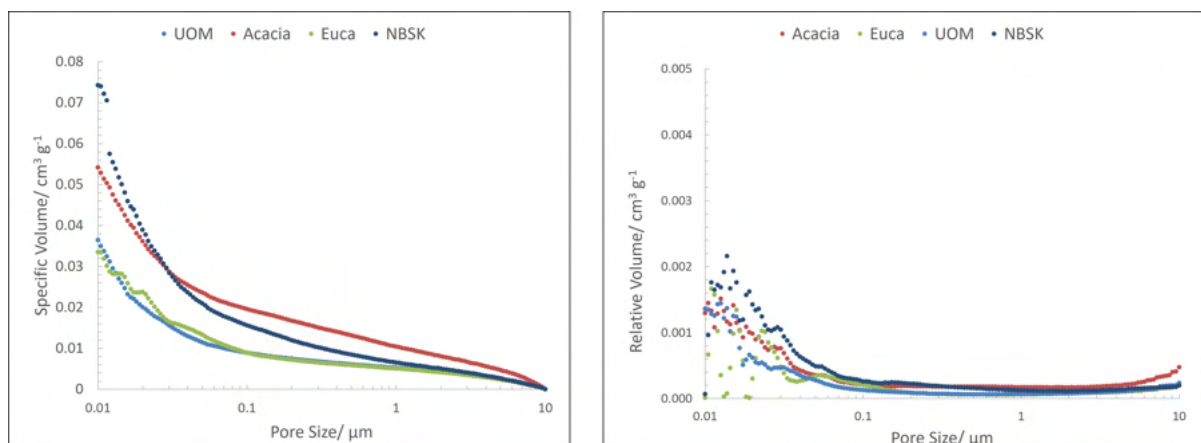


Fig. 6.15. Mercury porosimetry analysis of MFC films

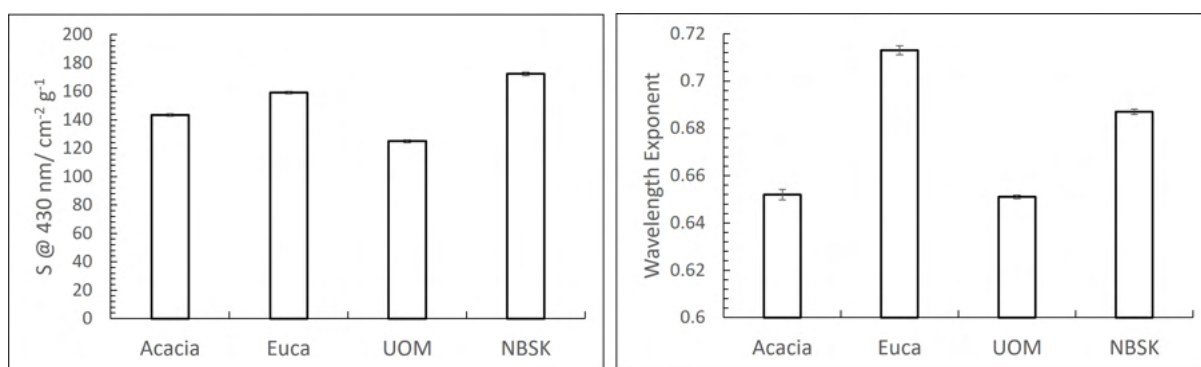


Fig. 6.16. Light scattering coefficient of MFC films at 430 nm and wavelength exponent of MFC films. Both parameters were averages of 9 measurements and error bars represent standard deviation.

Barrier Properties of MFC Films

Figure 6.17 shows the HVTR and HVP for MFC films. Clearly, the acacia MFC film showed higher HVTR and HVP than the other MFC films. However, there was little difference between the eucalyptus, University of Maine and NBSK MFC films, with variation between the results being greater than differences between the samples.

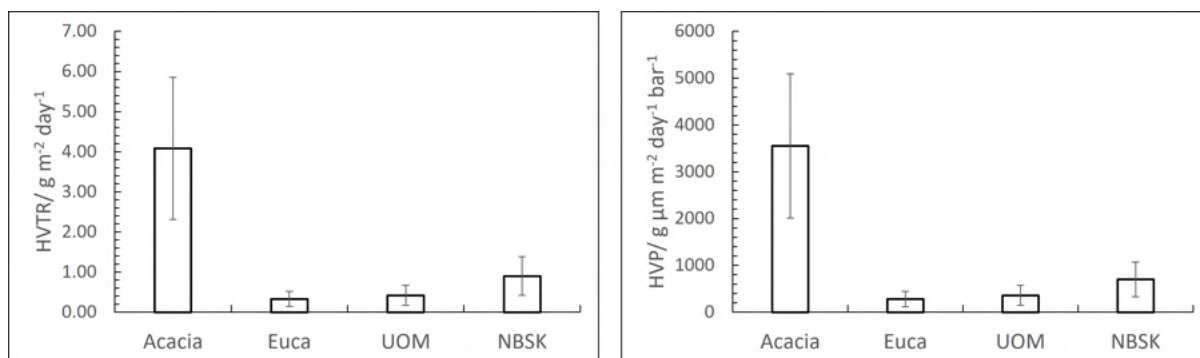


Fig. 6.17. Heptane vapour transmission rate (HVTR) and heptane vapour permeability (HVP) of MFC films. Heptane vapour pressure at 23°C was calculated using Antoine coefficients found in Yaws¹⁹³.

Figure 6.18 shows that the acacia and University of Maine MFC films had the lowest WVTR and WVP. Differences in water vapour barrier are likely to be related to differences in the chemical properties of the different pulp sources.

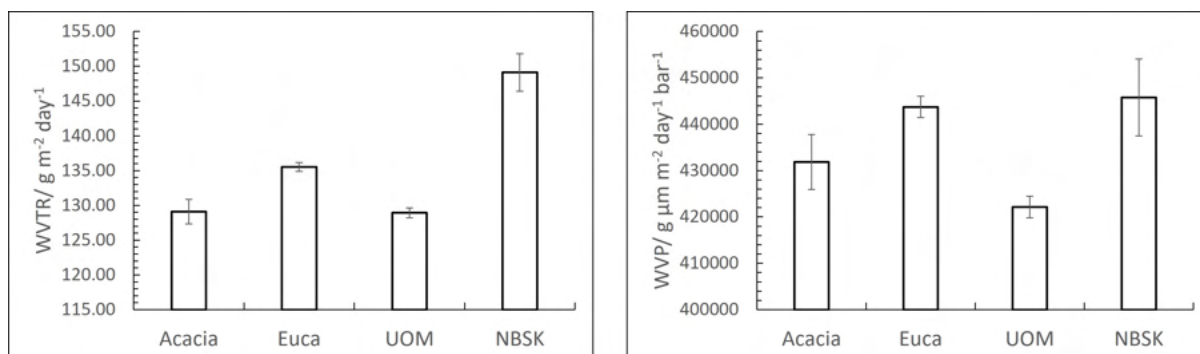


Fig. 6.18. Water vapour transmission rate (WVTR) and water vapour permeability (WVP) of MFC films. Water vapour pressure at 23°C was calculated using Antoine coefficients found in Yaws¹⁹³.

6.3.3 Surface Topography of MFC Coated Sheets

Figure 6.19 shows the surface profile of acacia MFC coated sheets. It is apparent that at 3 g m^{-2} , there is incomplete coverage of the base sheet with the MFC layer. At 6 g m^{-2} and above, there is much more effective coverage of the base sheet. Figure 6.20 shows the surface topography of the NBSK MFC coated sheets. The coverage at 3 g m^{-2} is much more uniform than the acacia coated sheet at the same coat weight. Large fibres are seen to cause a disturbance in the MFC coating layer, showing at a greater height than the rest of the surface for the higher NBSK coat weights.

Figure 6.21 shows the surface topography of eucalyptus MFC coated sheets. Fibre fragments are visible as protruding in height from the MFC coating, which indicates they may cause some

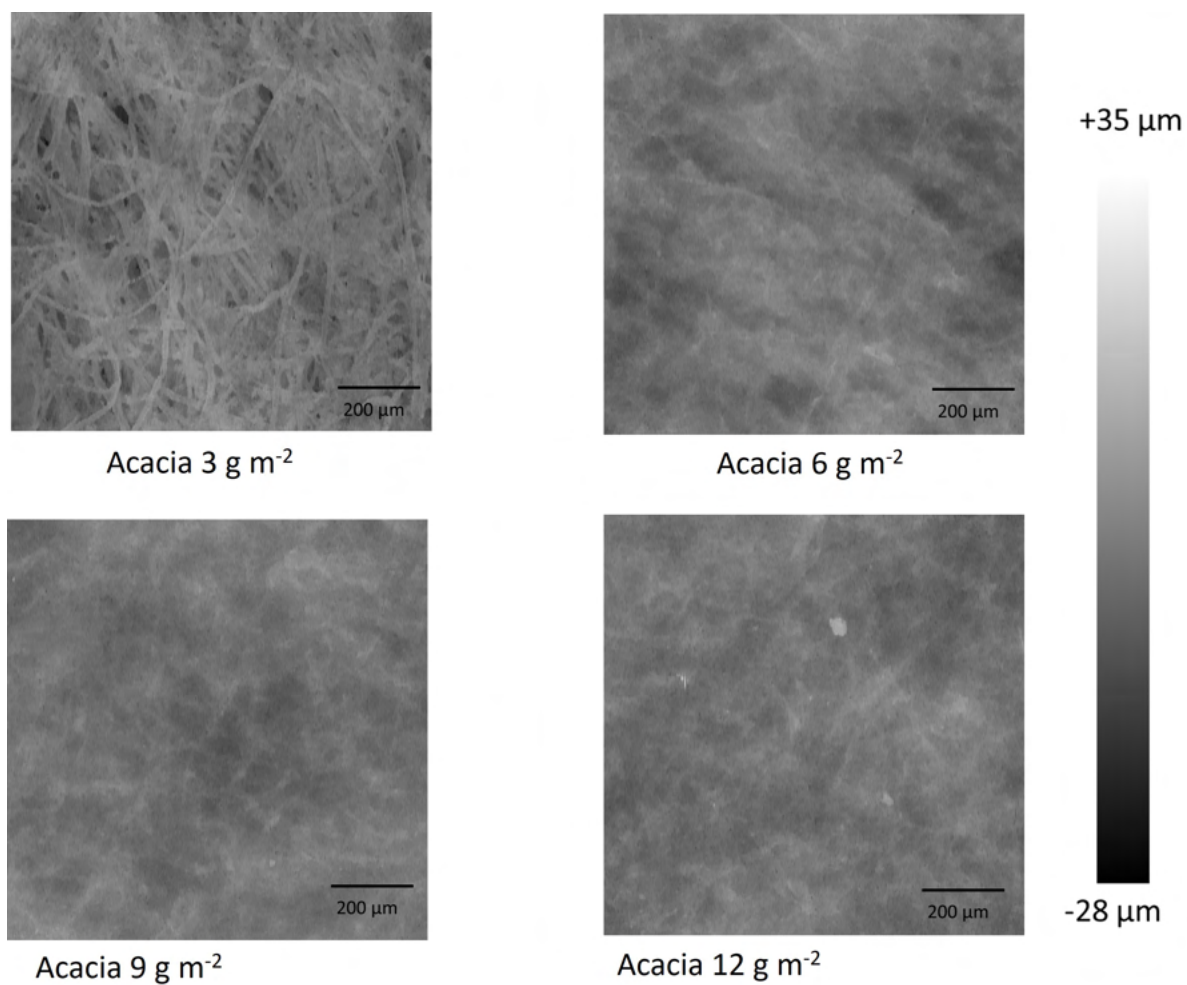


Fig. 6.19. Surface topography of acacia MFC coated sheets, measured with a laser interferometric profilometer.

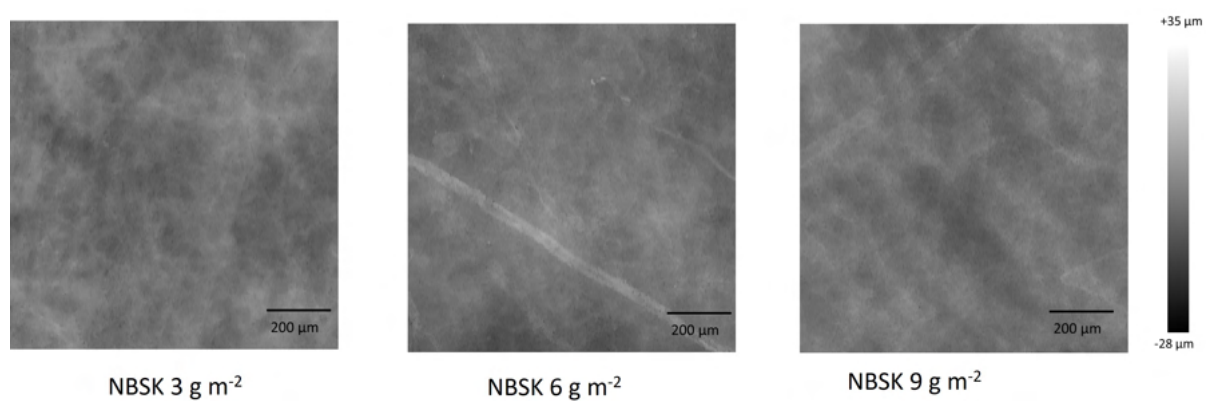


Fig. 6.20. Surface topography of NBSK MFC coated sheets, measured with a laser interferometric profilometer.

disturbance in the MFC layer. However, the fibre fragments are visibly narrower and shorter than the NBSK fibres observed in Figure 6.20.

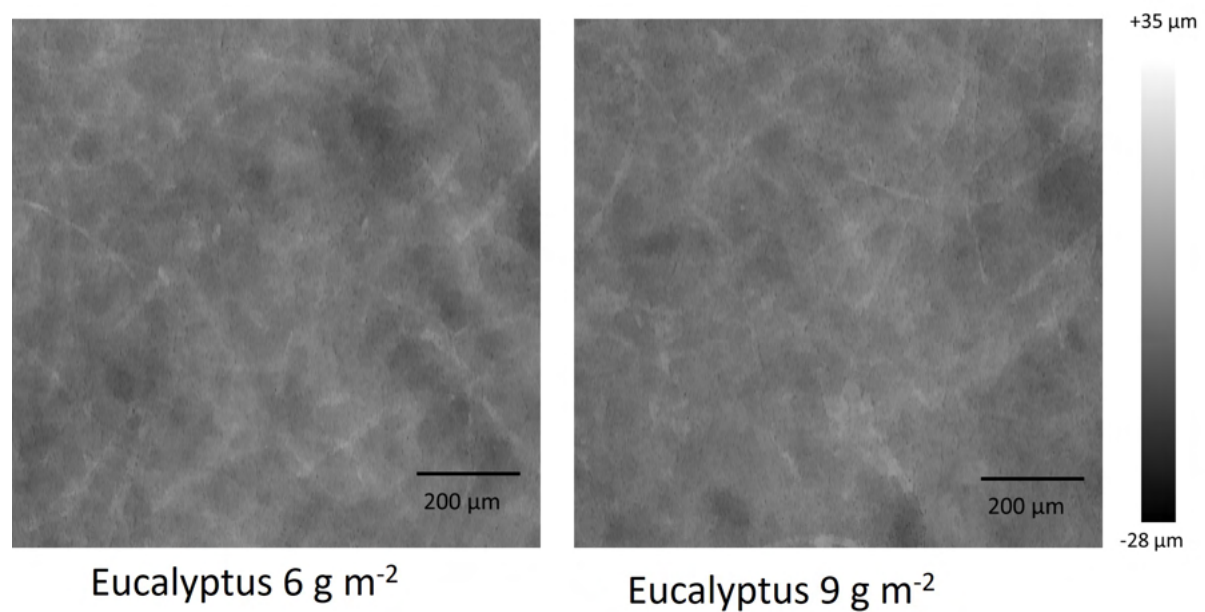


Fig. 6.21. Surface topography of Eucalyptus MFC coated sheets, measured with a laser interferometric profilometer.

Figure 6.22 shows the surface topography of the University of Maine MFC coated sheets. Some fibre disturbances can be observed but overall the coverage looks even with little disturbance from large fibres.

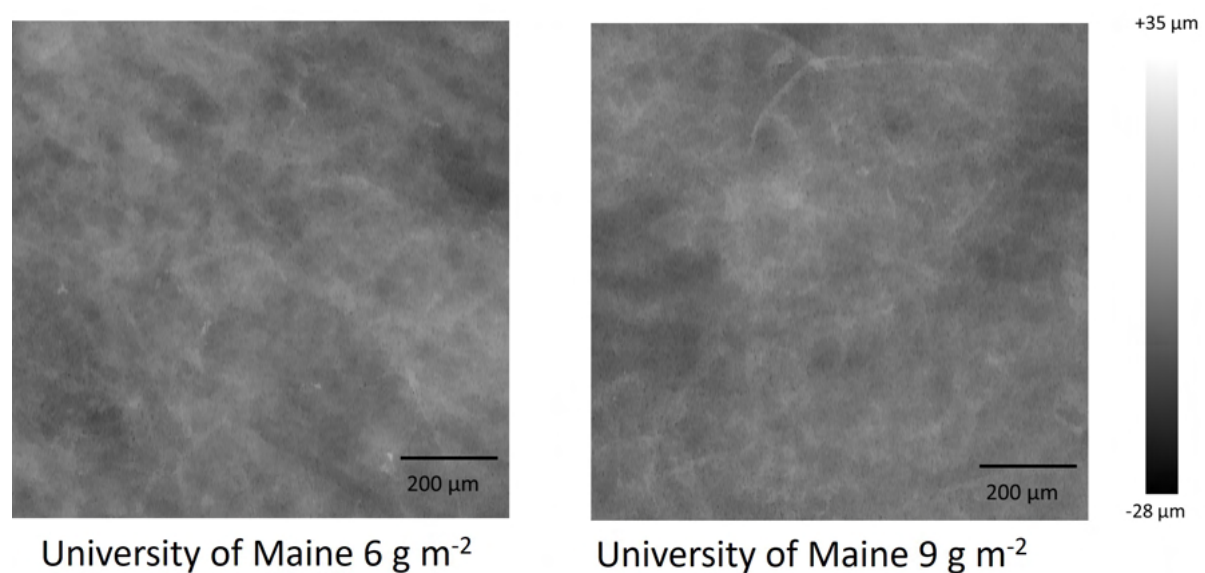


Fig. 6.22. Surface topography of University of Maine MFC coated sheets, measured with a laser interferometric profilometer.

6.3.4 Barrier Properties of MFC Coated Sheets

Bendtsen Porosity

Figure 6.23 shows the effect of increasing MFC coat weight on the Bendtsen porosity of MFC coated paper. Clearly, any MFC coating results in a significant decrease in Bendtsen porosity from the base sheet only. Increasing the MFC coat weight results in decreased Bendtsen porosity for the acacia, NBSK, and University of Maine MFC samples. This is a similar trend to that observed in Figure 4.7. The eucalyptus MFC sample was the most effective in reducing the Bendtsen porosity of the base sheet. MFC samples with a coat weight of 6 g m^{-2} and above were selected for HVTR testing since all samples showed a significant decrease in Bendtsen porosity.

The decrease in Bendtsen porosity for the acacia MFC coated sheets between 3 g m^{-2} and 6 g m^{-2} could be related to the increase surface coverage of the base sheet with an MFC layer visible in Figure 6.19. The Bendtsen porosity of the NBSK MFC coated sheet at 3 g m^{-2} is lower than that of the acacia MFC coated sheet. This could be linked to the difference in MFC surface coverage visible in Figure 6.19 and Figure 6.20. The NBSK MFC sample has a higher Bendtsen porosity at 6 g m^{-2} than the eucalyptus and University of Maine coated samples. This was an unexpected result since Chapter 5 suggested that increasing MFC fibrillation, measured through increasing FLT index, was an indication of improved barrier performance, and the NBSK MFC had a much higher FLT index than the eucalyptus MFC as seen in Table 6.1. However, Figure 6.20 shows that the NBSK MFC coated sheets showed significant disturbance from large fibres which was not visible in other MFC coated sheets. Large fibres were also present in the coated layers of homogenised MFC described in Chapter 5, where FLT index correlated well with barrier properties. However, in Chapter 5, the proportion of large fibres did not significantly vary during homogenisation so was more of a constant factor than in this case.

Grease Resistance

Figure 6.24 shows the effect of MFC coat weight on grease resistance, as measured using the Kit test described in Chapter 3, for the four selected MFC samples. Increasing MFC coat weight improves grease resistance, as was seen previously in Figure 4.10. The eucalyptus MFC samples produced coatings with the highest grease resistance. This was unexpected because Figure 5.22 showed that increasing FLT index led to improved grease resistance. However, this did agree with the trend in Bendtsen porosity results in Figure 6.23. Notably, the acacia MFC sample also formed coatings with superior grease resistance to the NBSK and University of Maine MFC, with the exception of 6 g m^{-2} .

Heptane Vapour Transmission Rate

Figure 6.25 shows the effect of MFC coat weight on the HVTR of MFC coated sheets for the four selected MFC samples. In accordance with Figure 4.8, increasing MFC coat weight decreases HVTR. Following the trend of Figure 6.23 and Figure 6.24, the eucalyptus MFC sample had the lowest HVTR at each coat weight by a significant margin. The acacia MFC had the highest HVTR at 6 g m^{-2} but was not significantly different from the University of Maine or NBSK samples at 9 g m^{-2} when accounting for variation in the measurements. Figures 6.23, 6.24, and 6.25 clearly show that the eucalyptus MFC formed the most effective barrier layers at a constant coat weight. Results presented in Chapter 5 implied that the following factors may indicate of whether an NBSK MFC sample would form effective barrier layers:

- A higher FLT index

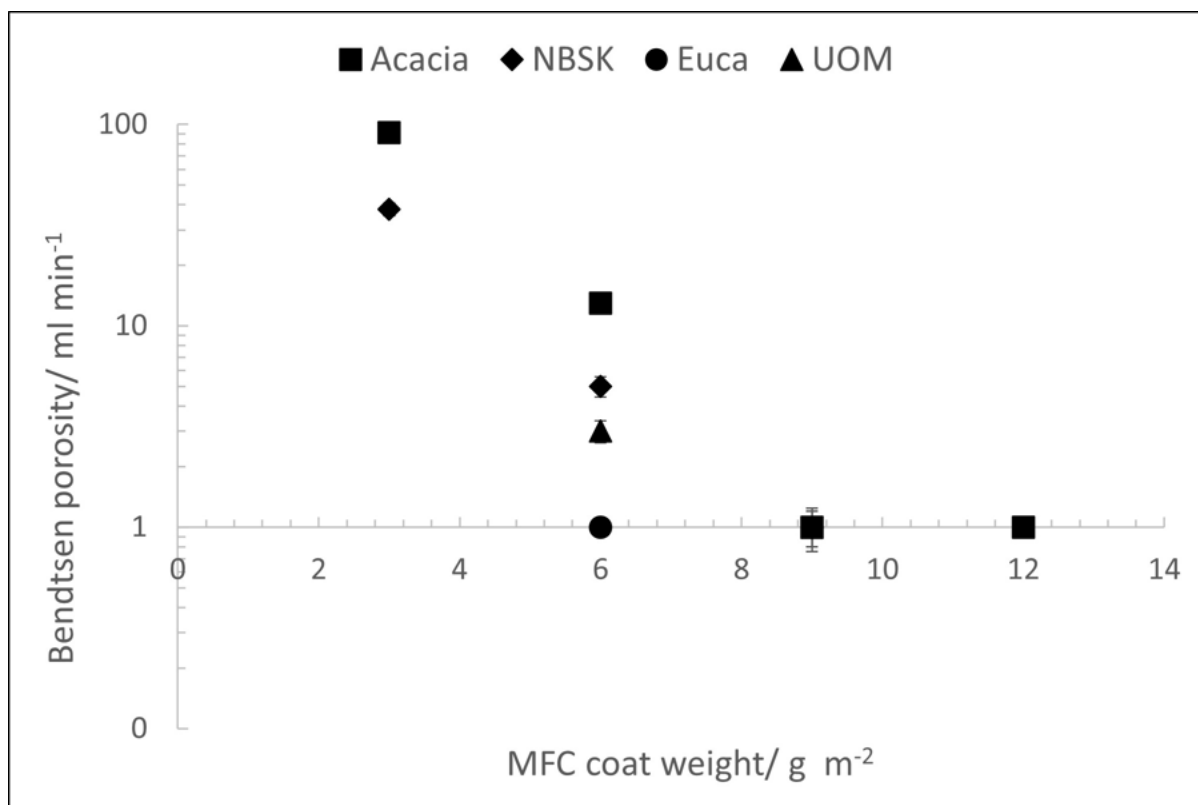


Fig. 6.23. The effect of MFC coat weight on Bendtsen porosity (plotted on a logarithmic y axis). Control base sheet filtered with water and dried had a Bendtsen porosity of $840 \pm 17 \text{ mL min}^{-1}$

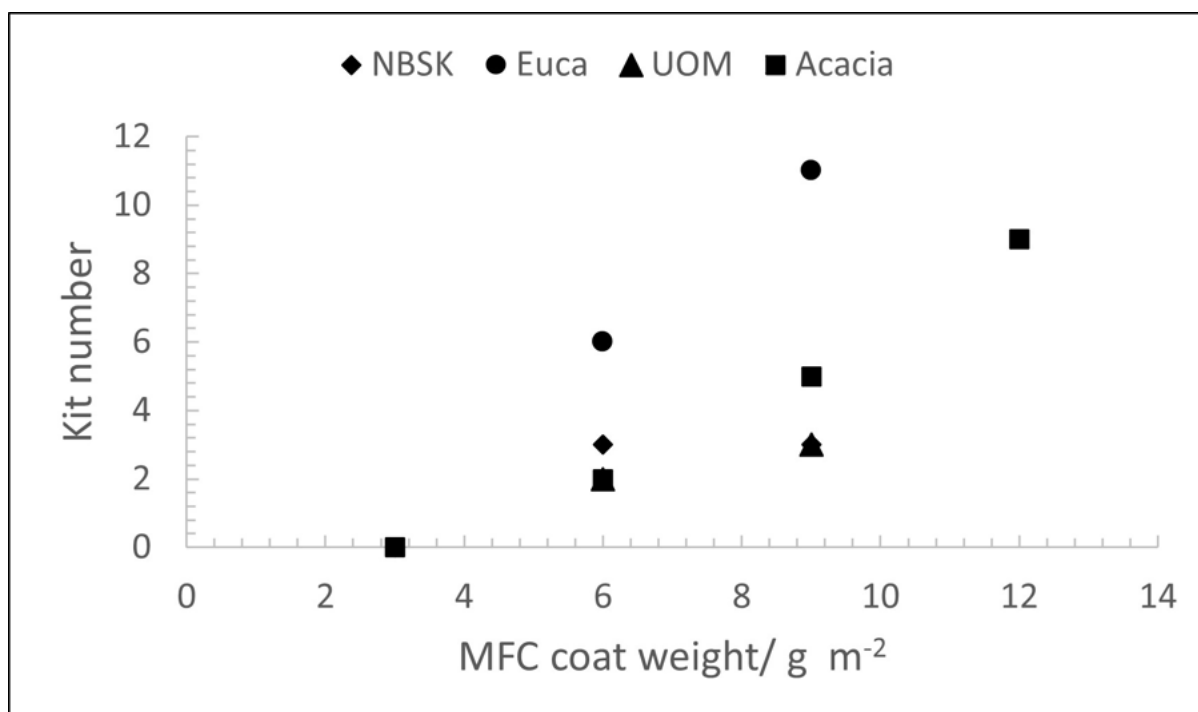


Fig. 6.24. The effect of MFC coat weight on Kit number. Control base sheet filtered with water and dried had Kit number 0.

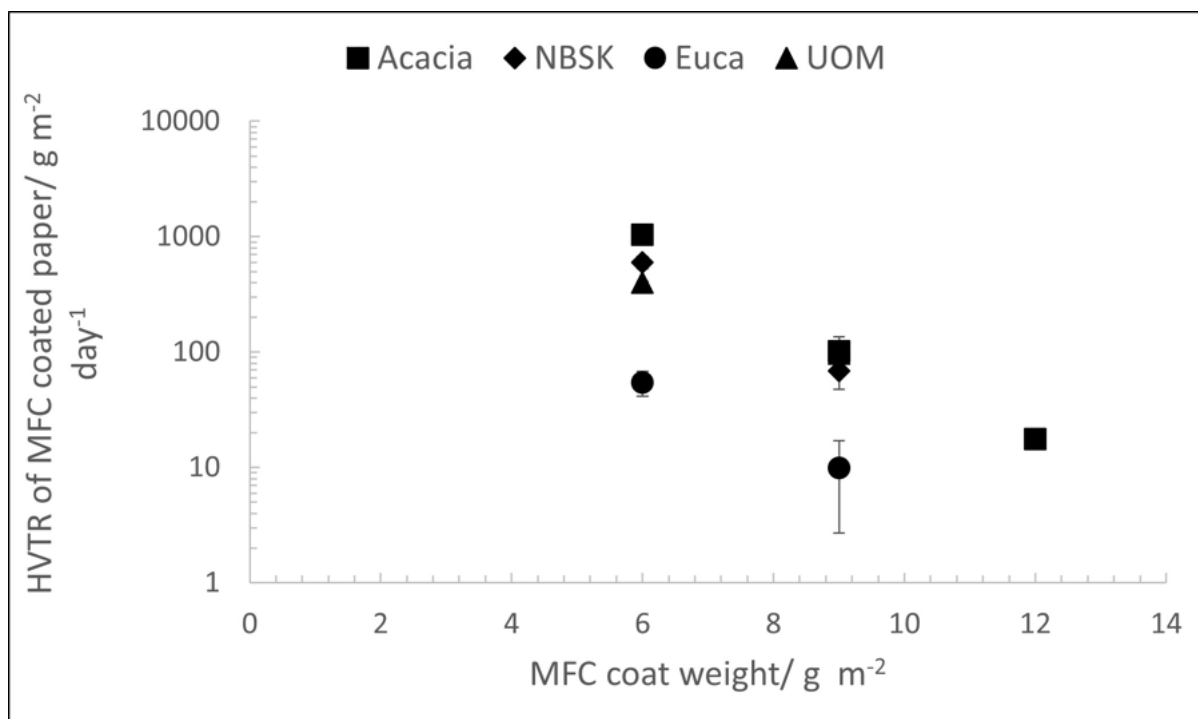


Fig. 6.25. The effect of MFC coat weight on HVTR (plotted on a logarithmic scale). Control base sheet filtered with water and dried had a HVTR of $2353 \pm 59 \text{ g m}^{-2} \text{ day}^{-1}$.

- A higher Fines A (for Kit values)
- A higher Fines B (for HVTR values)
- A lower Curl

Figure 6.26 shows that for a 9 g m^{-2} MFC coating, the eucalyptus sample performs the best even though the FLT is lower than two other samples. A decrease in Fines A and Curl leading to increased grease resistance could be interpreted but more data points would be required to verify this relationship. Figure 6.27 shows that there is also no definitive effect of FLT on HVTR. There may be some relation between increasing Fines A and Curl leading to increasing HVTR values but more MFC samples would be needed to consider this fully.

6.3.5 Further MFC Characterisation

The fact that the eucalyptus sample had a lower FLT than the University of Maine and NBSK MFC samples but superior grease and heptane vapour barrier properties when coated onto paper disagrees with the data from Chapter 5. This could be related to differences in the pulp types, since there could be a different relationship between the level of fibrillation and the relative bonded area of a sheet for different types of pulp, possibly influenced by hemicellulose content, fibre length, crystallinity, or degree of polymerisation. Therefore, another method to compare degree of fibrillation of different MFC samples was required.

SEM Imaging

The fibre analyser data suggests that the eucalyptus sample had a lower Fines A, and Fines B than the NBSK and University of Maine MFC samples, suggesting a lower level of fibrillation. However, the fibre image analyser functions through optical microscope image analysis. There could be finer cellulose material in the eucalyptus sample which is not visible. Therefore, the

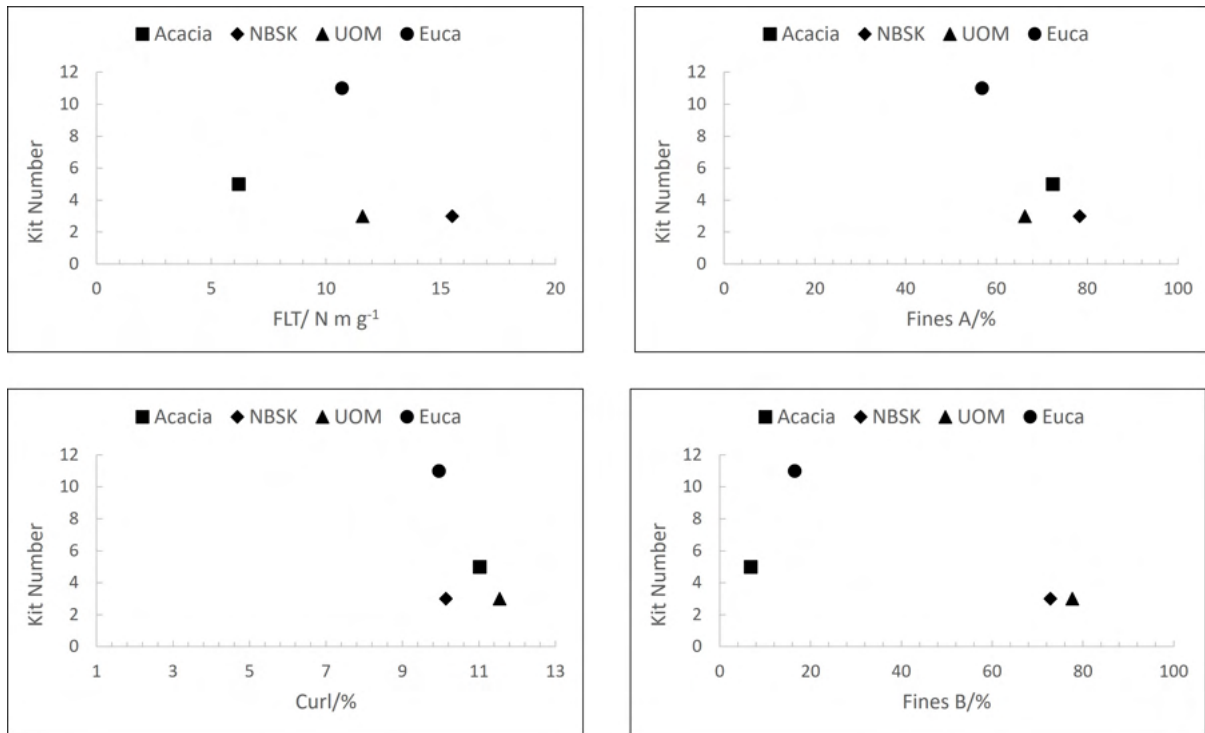


Fig. 6.26. The effect of FLT, Fines A, Curl, and Fines B of 9 g m⁻² MFC on Kit number

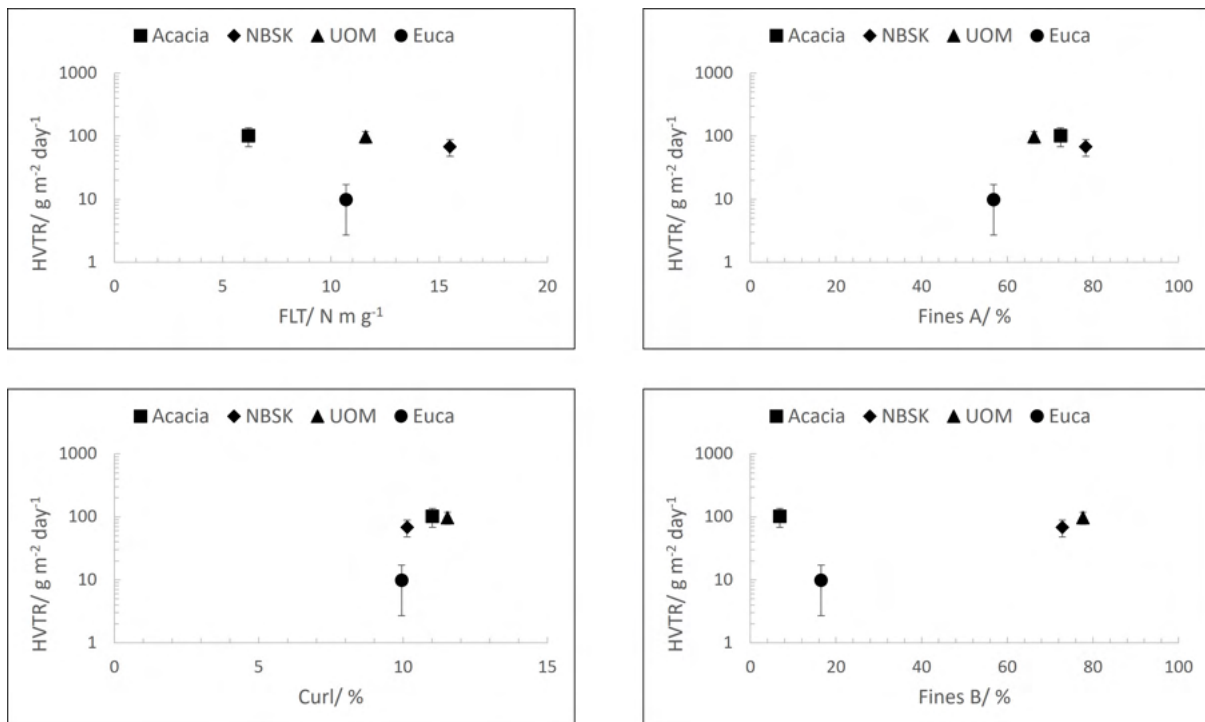


Fig. 6.27. The effect of FLT, Fines A, Curl, and Fines B of 9 g m⁻² MFC on HVTR (plotted on a logarithmic scale)

MFC samples were visualised through SEM, to understand more about the morphology of the fine cellulose material. Figure 6.28 shows SEM images of the three MFC samples. 20 images were taken per sample and a representative image was selected for each.

In all samples, images were taken showing large fibre fragments, fibril aggregates, some with a fine structure. The NBSK and UOM samples both showed networks of long fibrils, similar to the DIC optical microscopy images of the samples. The eucalyptus sample showed aggregates of fine material, forming a web like structure, suggesting there was some difference in the morphology of the materials. However, it is difficult to make any conclusive statements based on the SEM images due to the entanglement of fibrils, size polydispersity, and the fact that obtaining representative analysis of the fibrils through images would have required extensive time. It would be more beneficial to find a relatively fast quantitative method to allow comparison of the effectiveness of MFC samples as barrier layers so that many samples could be compared.

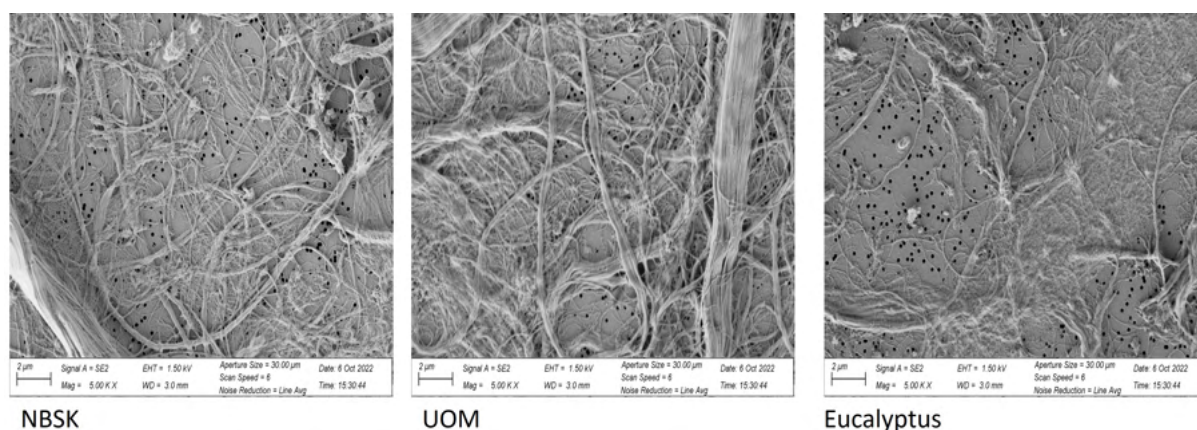


Fig. 6.28. SEM images of Pt sputter coated MFC samples from 1 mL of 0.001 wt% suspensions of MFC drained onto a 200 nm pore filter

6.4 | Discussion

Results from applications of MFC onto base paper showed that increasing MFC coat weight led to a decrease in air permeability, improvements in grease resistance, and lower HVTR. This shows that in some cases where obtaining a high degree of fibrillation is not practical, or a lower energy demand is required, a higher MFC coat weight can be used to obtain barrier properties. Therefore, the choice of MFC sample to use in an industrial coating process is likely to involve a balance of consideration of the rheology of a higher degree of fibrillation MFC potentially making the coating process more difficult, and the level of barrier properties required.

Chapter 5 showed that increasing FLT index of MFC samples correlated with improved grease resistance and decreased HVTR for 10 g m⁻² NBSK MFC coatings. However, in the present chapter, the eucalyptus MFC sample formed coatings with the highest grease resistance and lowest HVTR despite having a significantly lower FLT index than the NBSK sample. Furthermore, other parameters such as Fines B, Fines A, and Curl— which were shown in Chapter 5 to correlate well with barrier properties— did not appear to have an influence in the present chapter. SEM images of the eucalyptus MFC sample compared to the NBSK and University of Maine MFC samples showed that the eucalyptus MFC sample did not appear to contain a significantly higher fraction of nano-structured material. The NBSK and University

of Maine samples also showed higher viscosity and yield stress than the eucalyptus sample, indicating a higher degree of fibrillation, although this could also have been influenced by higher aspect ratio fibrils and may have been affected by the presence of large fibres.⁶⁰

Therefore, there appears to be other factors affecting the barrier properties of MFC coatings rather than increased degree of fibrillation measured through the FLT index or fibre image analyser parameters. The density of MFC films measured through digital micrometer shows that the eucalyptus MFC films had the lowest density despite forming MFC coatings with the most effective barrier properties. However, Figure 6.10 shows that there was some variation of thickness in the film, possibly caused by surface roughness. This surface roughness may have led to an over-estimation of the thickness of the films when measured using the digital micrometer. On the other hand, the mercury porosimetry data showed that there was little difference in pore volume below 10 μm between the MFC film samples, which suggests that the pore structure of the films are similar.

The HVTR and HVP of the eucalyptus, NBSK and University of Maine MFC films was similar, with only the acacia MFC film samples having a notably higher rate of heptane vapour transmission. This suggests that there may have been a difference in structure between the MFC films and MFC coatings. The MFC films were 50 g m^{-2} whereas the MFC coatings were in the range of 3- 12 g m^{-2} . Therefore, the MFC films were significantly thicker than the MFC coatings. Furthermore, the MFC coatings were presented on a rough, porous base sheet which may have affected the structure of the MFC layer. For example, there may have been an interface where some fine MFC material was lost into the base sheet or was filling in gaps between large fibres in the base sheet rather than forming a dense MFC layer.

Characterisation of MFC films showed that the NBSK MFC network contained large fibres. Laser height profile images of the MFC film surfaces showed that these large fibres caused a disturbance in the film. A disturbance from a large NBSK fibre is also seen in the laser height profile images of MFC coated paper. The eucalyptus MFC sample also contains fibre fragments but these are smaller than the NBSK fibres, possibly because of the different pulp types. Large fibres may have had more of an influence on the barrier properties of thin coating layers as opposed to thick MFC films. However, the University of Maine MFC sample does not contain large fibre fragments and still forms less effective barrier coatings than the eucalyptus MFC.

The present chapter contains only four MFC samples, and they are not only different degrees of fibrillation but the Fiberlean MFC samples are also made from different pulp types. Pulp type may have an effect on the relationship between measurement of degree of fibrillation and barrier properties. Therefore, the next part of the research project aimed to survey a large number of MFC samples from different pulp types to attempt to find a robust measurement of cellulose fibrillation to estimate barrier performance.

6.5 | Conclusions

The present chapter showed that increasing MFC coat weight resulted in improved barrier properties of different MFC samples, suggesting that increasing MFC coat weight could be a viable alternative to increasing degree of fibrillation as a method to obtain superior grease resistance and lower heptane vapour permeability. However, the results also showed a disagreement with Chapter 5, where a sample with a lower FLT, lower Fines B and lower Fines A than an NBSK MFC sample formed more effective barrier layers at a constant coat weight. MFC films made from the same samples showed that the NBSK MFC film was more dense than the eucalyptus MFC film, which suggested there may have been a difference in the structure of MFC coatings and films. Large fibres present in the NBSK MFC sample may have

been responsible for the poorer barrier properties of MFC films. However, it could also be the case that the fine fibrils resulting from homogenisation of the NBSK may have fallen into gaps between large fibres in the base sheet, preventing a dense film of MFC from forming on top of the sheet. Further work in the project aimed to further understand the effect of increasing fibrillation on barrier properties and whether pulp type also affected this relationship.

The present chapter involved the use of multiple characterisation techniques, exploring the morphology of the MFC, rheological properties of MFC suspensions, and structure of MFC films. There was no clear link from these data to the barrier properties of MFC coatings. However, this characterisation data helped to inform the overall conclusions of the chapter that although the NBSK and University of Maine MFC appeared to be finer MFC samples than the eucalyptus MFC sample, the barrier properties of the MFC coatings were not as effective. This may have been due to large fibre fragments, differences in pulp type, or may have been due to the porous structure of the base sheet.

Effect of Pulp Type and Degree of Fibrillation on the Barrier Properties of MFC

7.1 | Introduction

Previous work in the research project found that increasing the degree of fibrillation was initially beneficial to improve barrier properties. However, further research showed that a seemingly coarser eucalyptus MFC formed more effective barrier layers than a highly fibrillated NBSK MFC. Therefore, more research was needed to further understand the effect of fibrillation on barrier properties using a wide variety of MFC samples across different pulp types. The effect of large fibre fragments on the barrier properties of MFC coatings was also considered, since the highly fibrillated NBSK did contain large fibres which may have contributed to the comparatively weaker barrier properties shown in Chapter 6. Along with this, the possibility of loss of fine MFC material into the base sheet was studied by coating sequential layers of MFC on the paper surface to determine barrier properties could be improved by coating a layer of finer MFC as a pre-coat to coarser MFC.

7.2 | Experimental

7.2.1 MFC Samples

Table 7.1 shows the MFC samples used in this section of the thesis. The FLT index is given here to provide an indication of the degree of fibrillation of the samples, since Chapter 5 showed a relation with barrier properties. Other methods of characterisation of the MFC including fibre image analyser and optical microscopy are discussed in Section 7.3.1.

7.2.2 MFC Coatings and Films

MFC coatings were applied through vacuum filtration onto a commercial base paper, as described in Chapter 3 and Chapter 4. Four sheets were coated for each sample of MFC so that three separate HVTR measurements and two separate Kit measurements could be taken. MFC films were made in accordance with Chapter 3 with an added step of pouring the filtrate back through the film after film formation and allowing to drain again to ensure that any fine cellulose material that had passed through the mesh on the first drainage was incorporated into the film. Five films were made for each MFC sample. A smaller selection of MFC samples was used to make films than coatings as there was not enough MFC left of some of the samples used in the coatings as a significantly larger volume of sample was required to make films.

Table 7.1

Pulp type and FLT index of MFC samples used in the present thesis chapter

Pulp type	FLT index/ N m g^{-1}
NBSK	8.6
NBSK	8.6
NBSK	14.1
NBSK	14.7
University of Maine reference sample	11.6
UBSK	9.9
UBSK	12.3
UBSK	12.4
UBSK	12.8
UBSK	12.6
UBSK	12.9
UBSK	13.5
UBSK	10.9
Birch	6.9
Birch	8.2
Birch	11.4
Birch	14.3
Acacia	5.7
Acacia	8.2
Acacia	9.2
Acacia	10.7
Eucalyptus	7.1
Eucalyptus	9.0
Eucalyptus	10.7
Eucalyptus	11.2
Eucalyptus	14.6
Eucalyptus	16.6
Unbleached Eucalyptus	9.2
Unbleached Eucalyptus	10.6
Unbleached Eucalyptus	12.7

Table 7.2

Description of MFC samples used in the multiple layers study

Label	Pulp type	Fines B/ %
E1	Eucalyptus	35.76
E2	Eucalyptus	70.93

7.2.3 Large Fibre Blends

To understand the effect of large, unfibrillated fibres on the barrier properties of MFC coatings, unprocessed eucalyptus fibres were added into the FLT 10.7 eucalyptus MFC sample which was shown to have excellent barrier performance in Chapter 6. The large fibres were prepared by soaking 100 g of bleached eucalyptus pulp in 10 L of filtered tap water for 15 hours. Following this, the pulp was broken into smaller pieces by hand and a further 10 L of filtered tap water was added to the mixture. The fibres were then dispersed by passing the mixture two times through a Messmer benchtop disintegrator. The consistency of the pulp was measured and diluted to 0.3%. The CSF of the pulp fibres was 611 mL, calculated from the mid point of two measurements.

Four MFC coating samples were made up and diluted to 0.5 wt% with filtered tap water. The first was the eucalyptus MFC sample with an FLT of 10.7 N m g⁻¹, then samples with increasing wt% of large fibres were added so that there were 5 wt%, 10 wt% and 15 wt% large fibres by total dry weight percentage of the material. The solids content of the coating samples was then measured so that an accurate coat weight could be applied.

7.2.4 Multi Layer Coatings

To understand whether the loss of fine cellulose material into the base sheet was contributing to the less effective barrier layers observed for MFC samples with a high proportion of fine material, two layers of MFC were applied to a base sheet in 2 g m⁻² layers to reach a total of 4 g m⁻². The MFC was diluted with tap water to 0.04 % solids before being poured onto the base sheet. Water from the first MFC coating was left to completely drain before the second MFC layer was applied.

The two MFC samples used in this part of the study are shown in Table 7.2. To understand whether MFC with a high proportion of fine material is a less effective barrier layer due to loss of fine cellulose into the base sheet, a low and high Fines B samples were selected. E1 and E2 correspond to Eucalyptus FLT 14.7 and 16.6 N m g⁻¹ in Table 7.1. The MFC was applied as single 4 g m⁻² layers for both samples as a reference point. The same MFC samples were also coated as two 2 g m⁻² layers as a reference point to understand how applying the MFC in two individual layers affects the barrier properties of the coated paper. Table 7.3 shows the structures of coatings of multiple layers of MFC used in the present study.

7.3 | Results

7.3.1 MFC Characterisation

Fibre Analyser

Figure 7.1 shows the relation between Fines A and Fines B for MFC samples used in the present thesis chapter. Chapter 5 showed that Fines B appeared to be an important parameter in barrier properties of MFC coatings and corresponded with increasing fibrillation observed in

Table 7.3

Structure of different coatings made for investigation of multiple layers of MFC

Coating structure	Layer weights/ g m^{-2}
E1	4
E1	2 + 2
E2	4
E2	2+ 2
E2 + E1	2+2
E1 + E2	2 + 2
E1	2
E2	2

optical microscope images. Therefore, the MFC samples selected showed a range of fibrillation levels from low to high Fines B and Fines A.

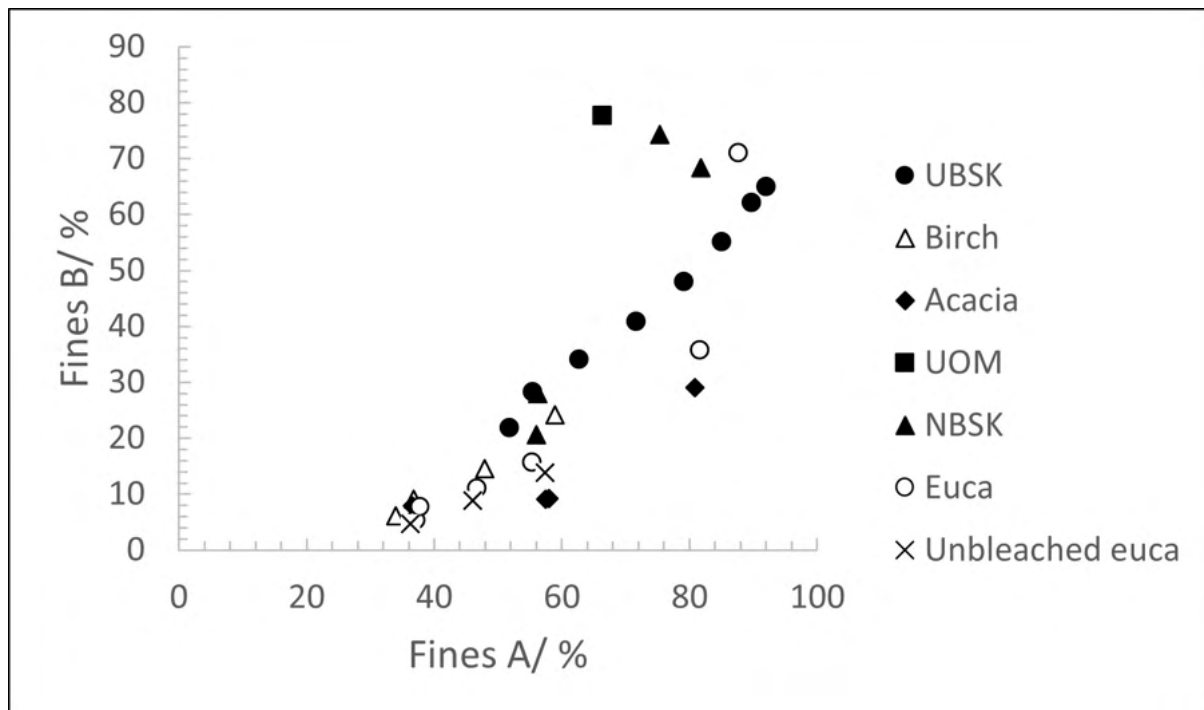
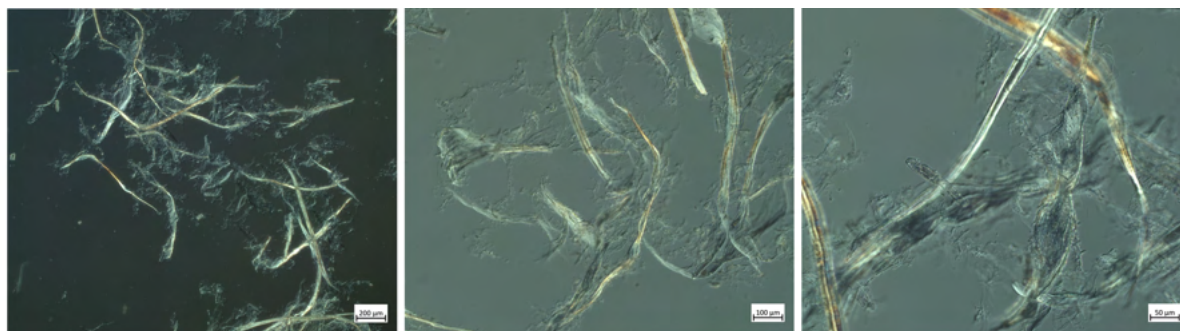


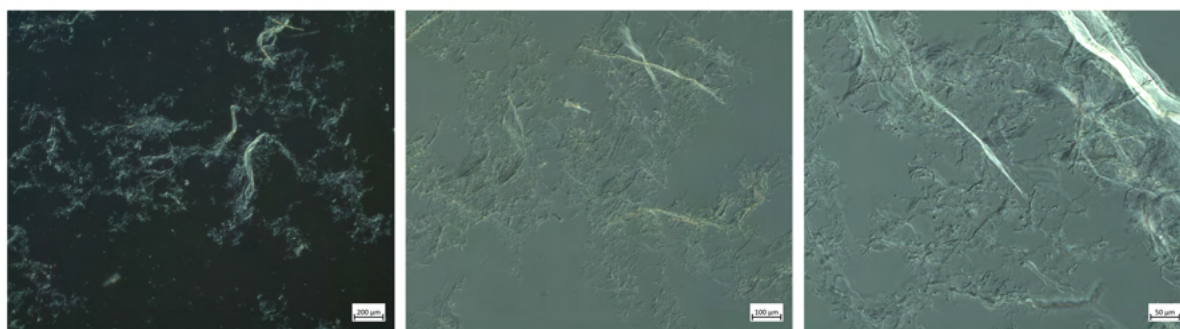
Fig. 7.1. Relation between Fines A and Fines B for MFC samples used in the present thesis chapter

Optical Microscopy

Figure 7.2 to Figure 7.6 show optical microscope images of MFC used in this thesis chapter. A low and high level of fibrillation was selected for optical microscope imaging for each pulp type, determined by an increase in FLT index. For the UBSK samples, the highest energy MFC had a lower FLT index. This sample is also included in the images. The NBSK samples had previously been imaged in Chapter 5. The NBSK samples used in the current study are those ground at $3000 \text{ k W h t}^{-1}$, $4500 \text{ k W h t}^{-1}$, $4000 \text{ k W h t}^{-1} + 400 \text{ bar}$ homogenisation and $400 \text{ k W h t}^{-1} + 1000 \text{ bar}$ homogenisation.

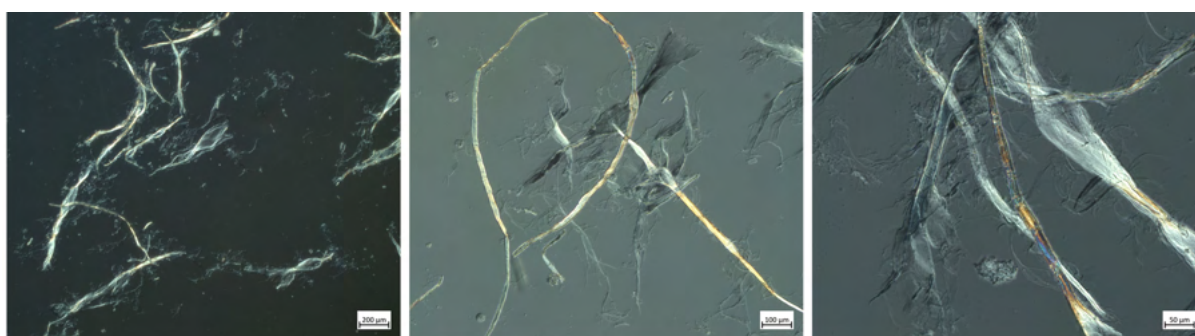


Unbleached eucalyptus, FLT 9.2 N m g⁻¹

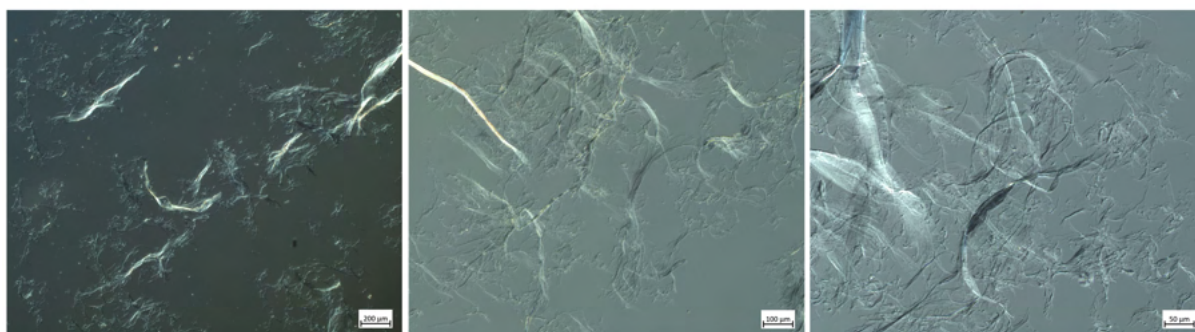


Unbleached eucalyptus, FLT 12.7 N m g⁻¹

Fig. 7.2. DIC optical microscope images of unbleached eucalyptus MFC at 0.08 wt% in aqueous suspension



Birch, FLT 6.9 N m g⁻¹



Birch, FLT 14.3 N m g⁻¹

Fig. 7.3. DIC optical microscope images of birch MFC at 0.08 wt% in aqueous suspension

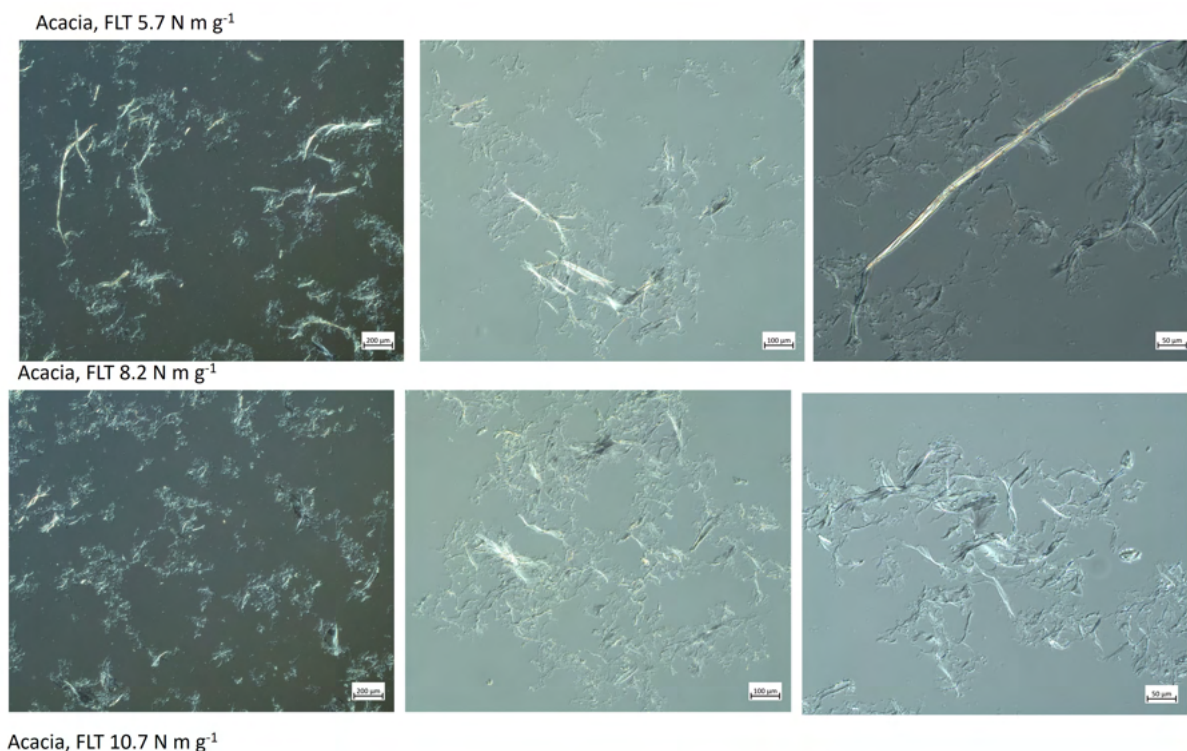


Fig. 7.4. DIC optical microscope images of acacia MFC at 0.08 wt% in aqueous suspension

7.3.2 MFC Coated Sheets

Visual Appearance of Sheets

Figure 7.7 shows the visual appearance of sheets coated with 6 g m⁻² of UBSK MFC with increasing grinding energy. It is apparent that as the grinding energy increases, the formation of the MFC layer becomes more irregular and flocculated. UBSK MFC coatings were later repeated to investigate if this irregular layer was seen again. Figure 7.8 shows that when increasing grinding energy, the formation of the MFC layer became more irregular again. This may have contributed to the irregular relationship between increasing degree of fibrillation and barrier properties for the UBSK MFC seen in Figure 7.12. It is possible that this irregular pattern is pattern of the vacuum through the wire mesh that the sheet was resting on. Figure 7.9 shows the scanned images of unbleached eucalyptus MFC coated sheets. There were large splinters of wood in the MFC suspension, not visible until the MFC coatings were applied. These wood splinters are likely to be bits of pulp that did not get processed into kraft pulp. These splinters of wood may have caused irregularities in the barrier properties of the MFC layers.

Laser Profilometry of Coated Sheets

Figure 7.10 shows the interferometric laser profilometry image of the surface of MFC sheets for the different pulp types. The highest and lowest FLT MFC samples are shown in Table 7.10. In the case of acacia, birch, eucalyptus and unbleached eucalyptus, increasing the process intensity to increase FLT has resulted in a more even surface coverage with fewer large fibres. In the case of the NBSK coatings, large fibres can be seen within the MFC coating.

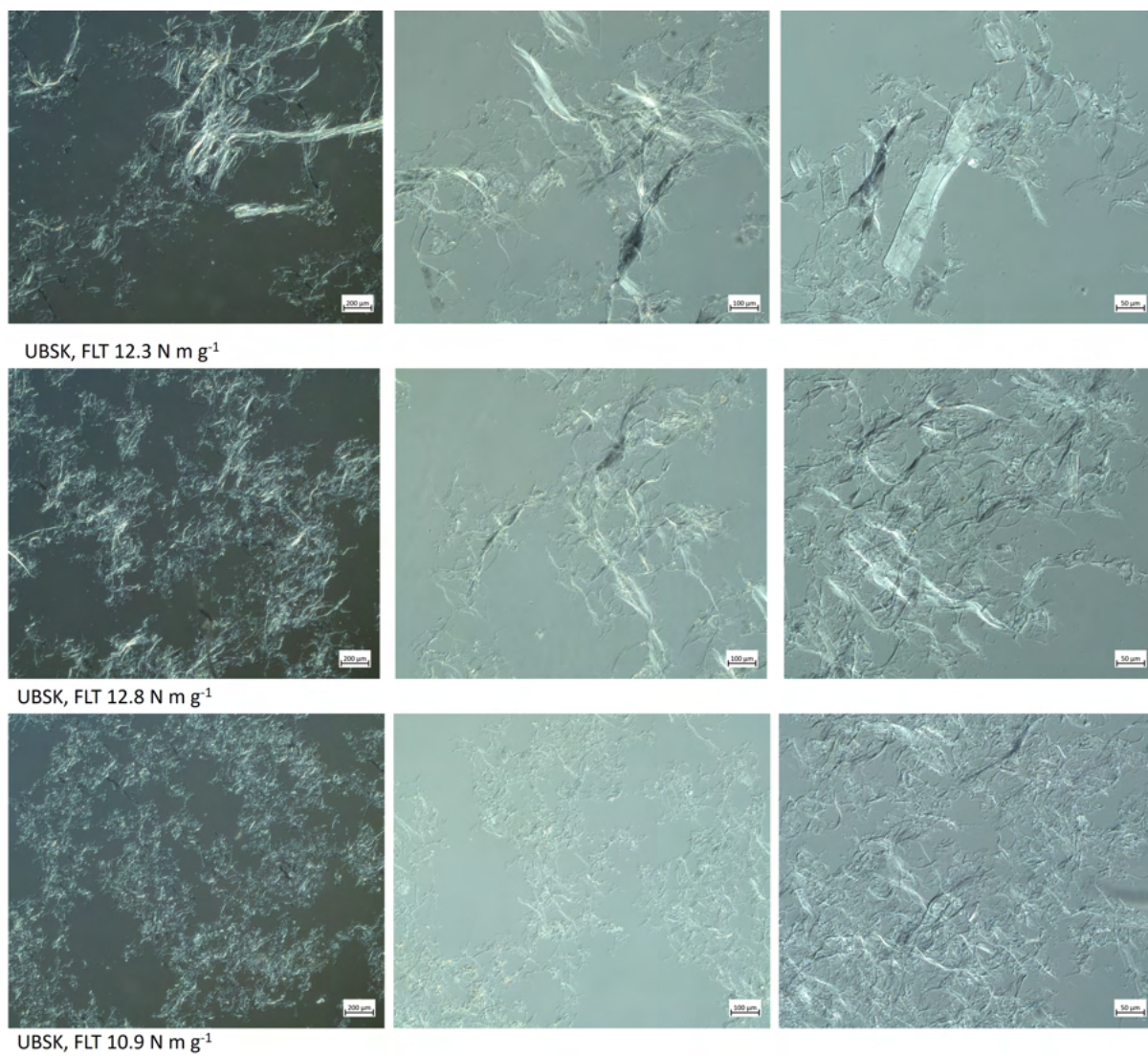


Fig. 7.5. DIC optical microscope images of UBSK MFC at 0.08 wt% in aqueous suspension

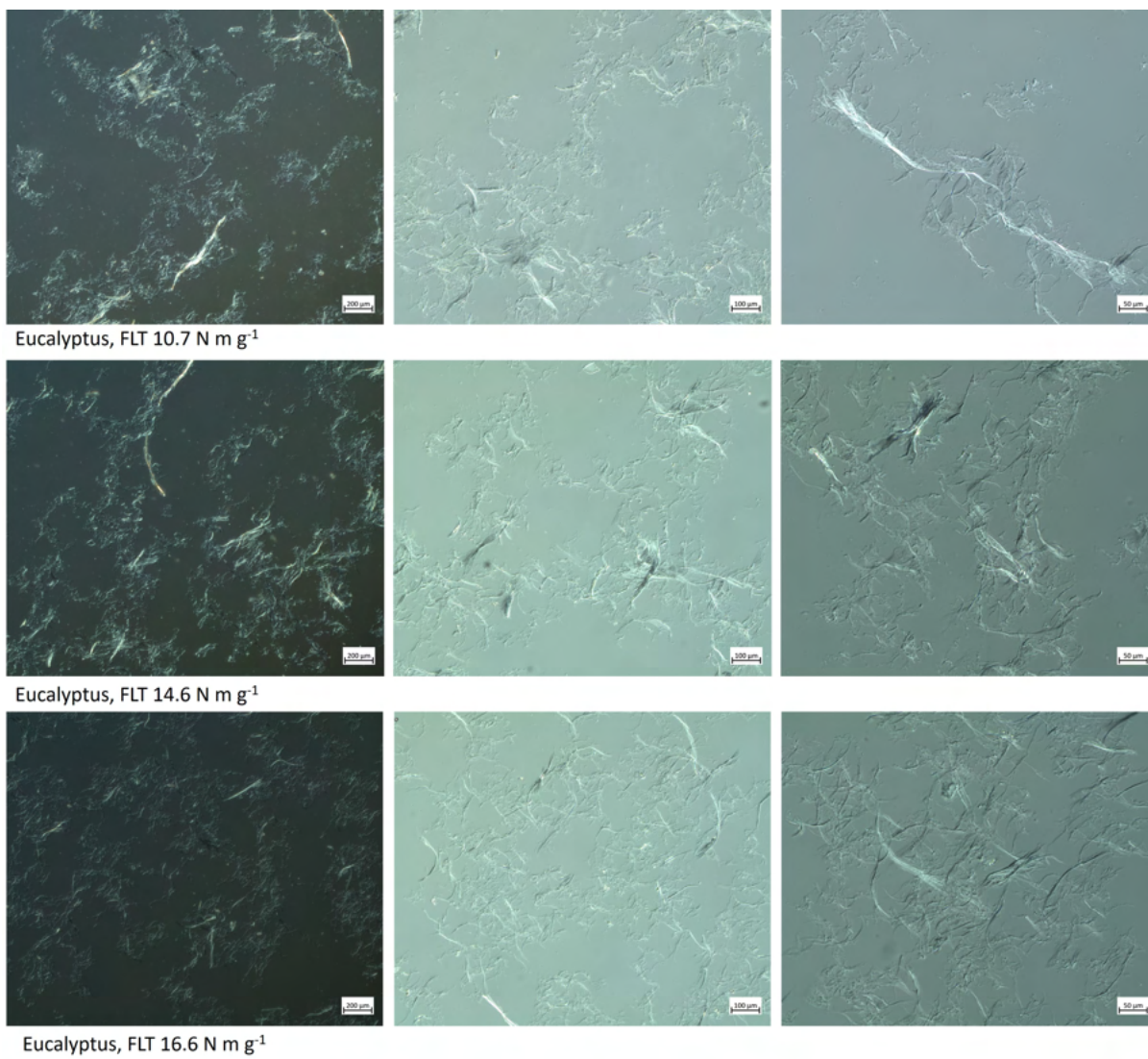


Fig. 7.6. DIC optical microscope images of eucalyptus MFC at 0.08 wt% in aqueous suspension

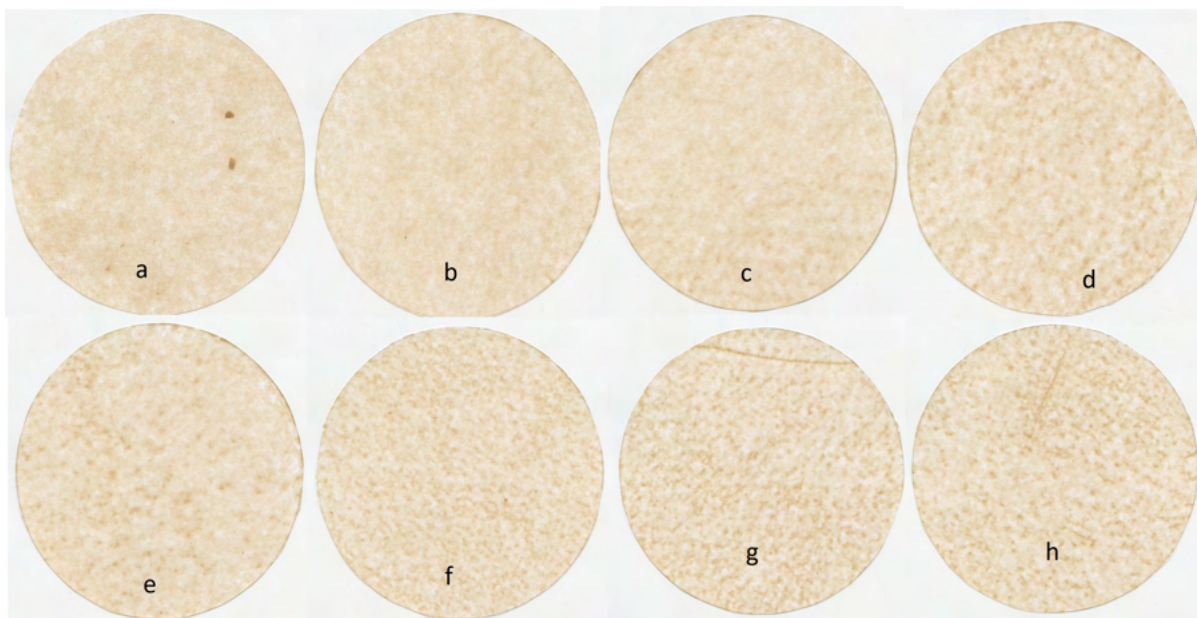


Fig. 7.7. Scans of UBSK MFC coated sheets with increasing grinding energy in increments of 500 k W h t^{-1} from a) $2500 \text{ k W h t}^{-1}$ to h) $6000 \text{ k W h t}^{-1}$

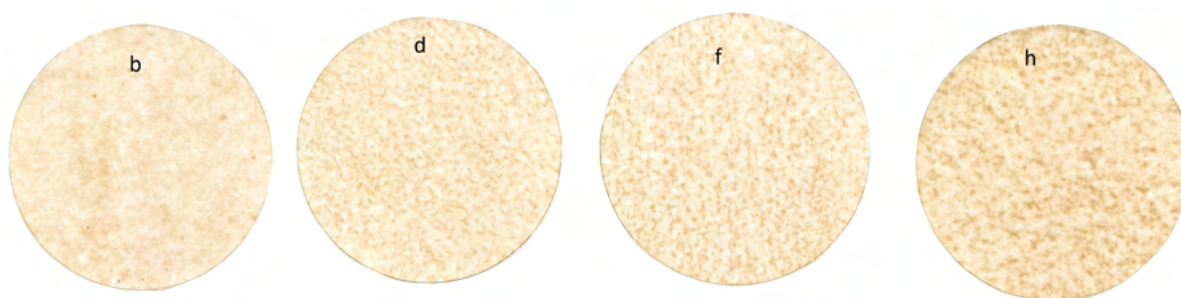


Fig. 7.8. Scans of UBSK MFC coated sheets from a separate round of coating UBSK MFC. Labels correspond to Figure 7.7

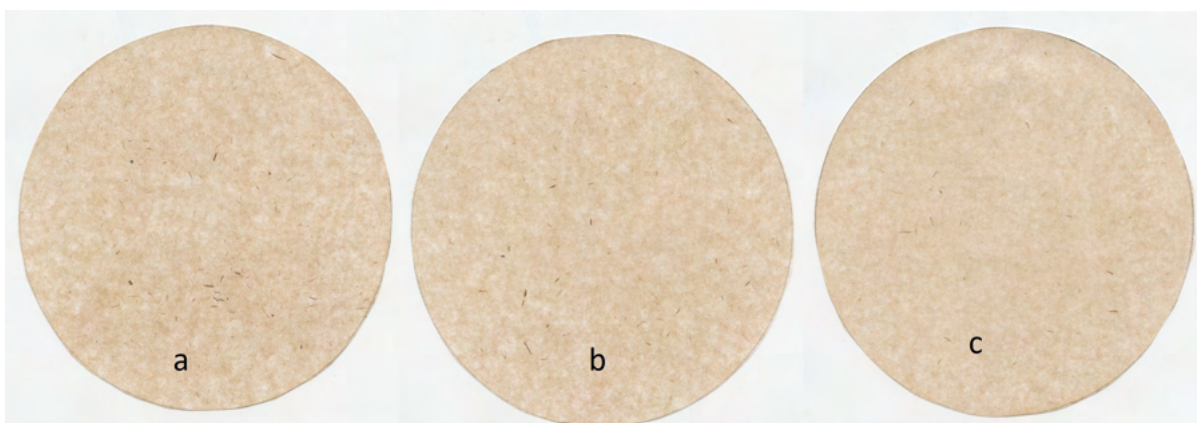


Fig. 7.9. Scans of Unbleached Eucalyptus MFC coated sheets with increasing grinding energy from a) $1250 \text{ k W h t}^{-1}$, b) $2250 \text{ k W h t}^{-1}$, c) $4500 \text{ k W h t}^{-1}$

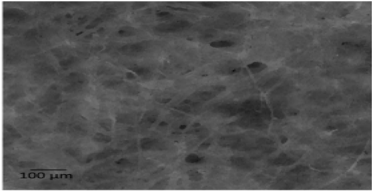
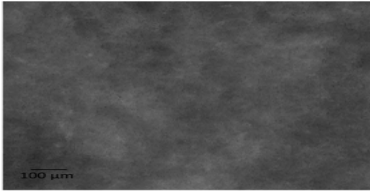
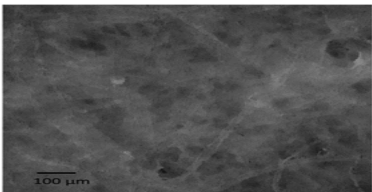
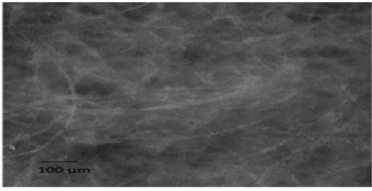
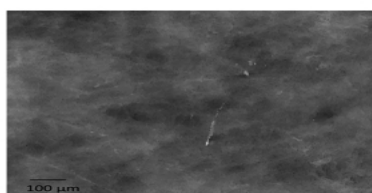
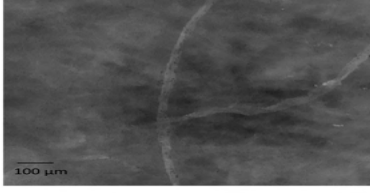
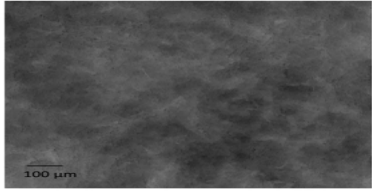
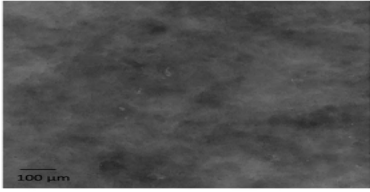
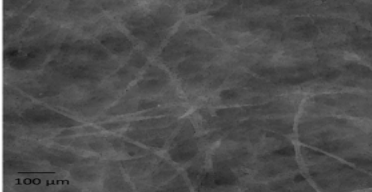
Pulp Type	Lowest FLT MFC coated onto base sheet	Highest FLT coated onto base sheet
Acacia		
Birch		
Eucalyptus		
NBSK		
UBSK		
Unbleached eucalyptus		

Fig. 7.10. Interferometric laser profilometer images of the surfaces of MFC coated sheets.

Air Permeability

Figure 7.11 shows the Bendtsen porosity of sheets coated with 6 g m^{-2} of MFC as a function of the FLT index of the MFC. There is a general decrease in Bendtsen porosity with increasing FLT index for each pulp type. The exception to this observation is that the highest FLT eucalyptus sample has a higher Bendtsen porosity than lower FLT eucalyptus samples. The difference between the two eucalyptus MFC samples is between 0 and 4 mL min^{-1} . Results from previous chapters suggested that effective barrier layers have Bendtsen porosity results of 1 or 0 mL min^{-1} . This suggests there may have been a significant difference in the barrier properties between these eucalyptus samples, likely due to differences in the morphology of the MFC samples.

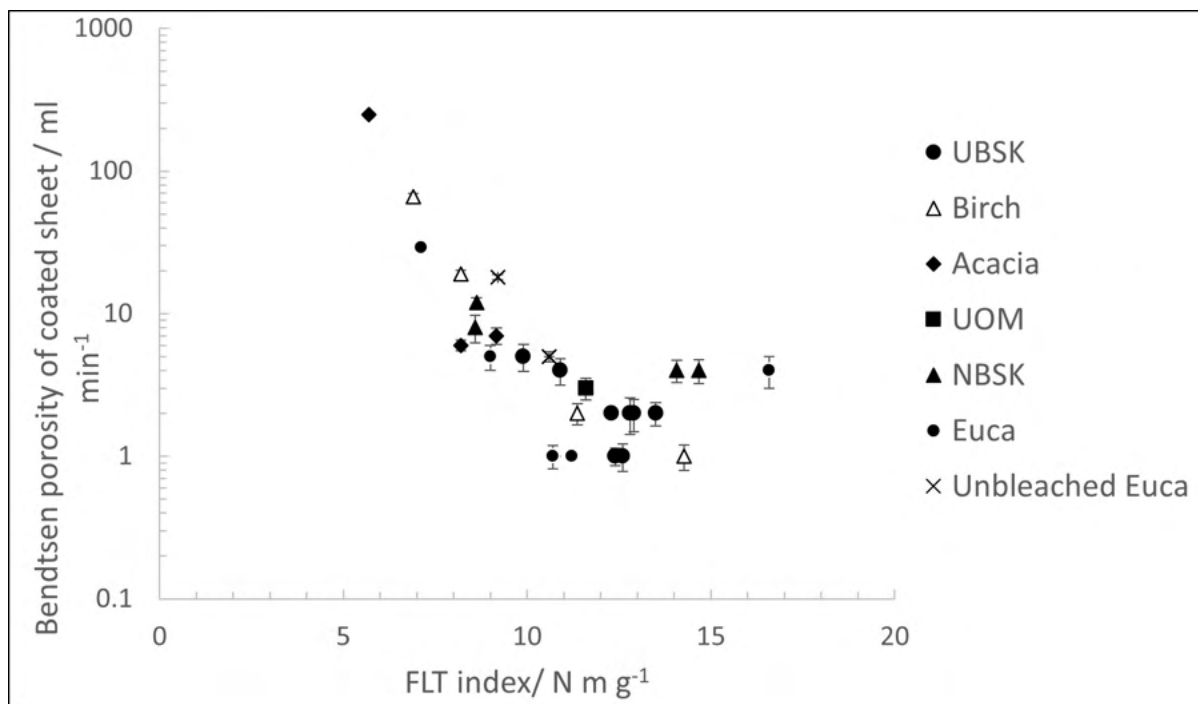


Fig. 7.11. Bendtsen porosity of sheets coated with 6 g m^{-2} of MFC as a function of the FLT index of the MFC.

Heptane Vapour Transmission Rate

Figure 7.12 shows the HVTR of sheets coated with 6 g m^{-2} of MFC as a function of the FLT index of the MFC. Similar to the Bendtsen porosity data, there is a general decrease in HVTR as the FLT index of the MFC increases for each pulp type with the exception of higher FLT UBSK samples. This may be related to the poor formation of the MFC layer observed in Figure 7.7. Similar to the Bendtsen porosity, there is an increase in measured HVTR for the highest FLT eucalyptus sample. The corresponding non-homogenised eucalyptus sample with an FLT index of 14.6 N m g^{-1} had a drainage time of $289 \pm 2 \text{ s}$ when coating MFC onto the base sheet. The homogenised eucalyptus sample with an FLT of 16.6 N m g^{-1} had a drainage time of $57 \pm 3 \text{ s}$. This suggests that there may have been a greater proportion of fine cellulose material in the homogenised eucalyptus samples which may have penetrated into the base sheet, resulting in less MFC remaining on the surface and a greater HVTR and air permeability. This result was based on the average of three separate sheets which suggests the higher HVTR value was not due to a defect in a coating.

Figure 7.13 shows the relation of HVTR against the fibre image analyser parameters Fines A, Fines B and Curl. It is apparent that there is little relationship between Curl and HVTR, in

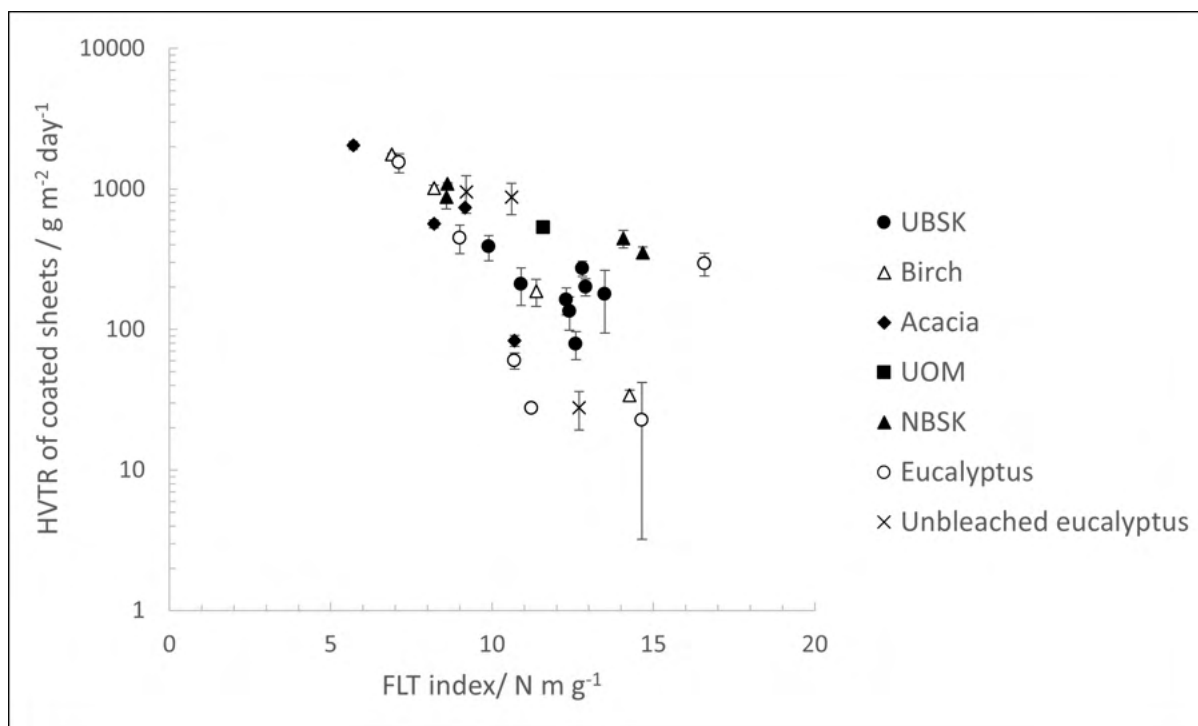


Fig. 7.12. HVTR of sheets coated with 6 g m^{-2} of MFC as a function of the FLT index of the MFC.

contrast to the results in Chapter 5. However, for birch, unbleached eucalyptus and eucalyptus, there is a decrease in HVTR with increasing Fines A with the exception of the homogenised eucalyptus sample. Similarly for Fines B, there is a decrease in HVTR with increasing Fines B for unbleached eucalyptus, eucalyptus, birch and acacia with increasing Fines B. However, there appears to be an increase in HVTR at when Fines B increases above 50%. This could further support the argument that fine cellulose material can fall into pores in the base sheet and therefore less MFC remains on top of the sheet.

Grease Resistance

Figure 7.14 shows the effect of the FLT index of MFC on the grease resistance of MFC coated sheets. The UBSK MFC samples show a large variation in measured Kit number, seen in large error bars. This could be related to the uneven formation of the MFC layers seen in Figure 7.7. There appears to be an increase in Kit number with increasing FLT index for eucalyptus, acacia, birch and unbleached eucalyptus MFC initially, but after an FLT index of 11, the Kit number appears to decrease. This shows a similar trend to heptane vapour transmission rate measurements where an increase in HVTR at high FLT index is seen for the eucalyptus sample. This further suggests that if an MFC sample contains a high proportion of fine material, it may form less effective barrier coatings.

Figure 7.15 shows the relation between the Kit number of MFC coated sheets and fibre image analyser parameters Fines A, Fines B and Curl. There is little relation in this case between any of these parameters and the grease resistance of the MFC coated sheets. This is a difference from the heptane vapour barrier properties which did show relations between Fines A and Fines B with HVTR. This could be because the HVTR measures the diffusion rate of heptane vapour over an area of 0.00321 m^2 whereas the Kit test measures whether an oil droplet will penetrate through a small area of the sheet. Therefore, if the droplet of oil lands on a defect in the sheet, this will result in penetration of the oil through the sheet. This differs from the

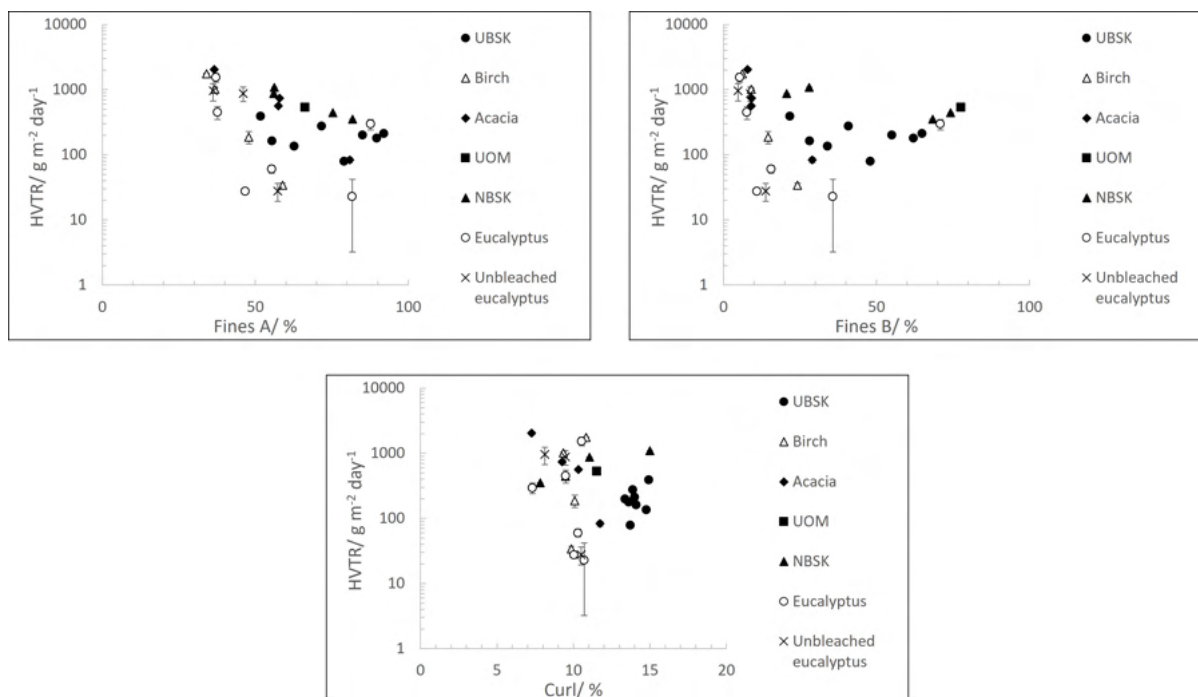


Fig. 7.13. HVTR of sheets coated with 6 g m^{-2} of MFC as a function of the FLT index of the MFC.

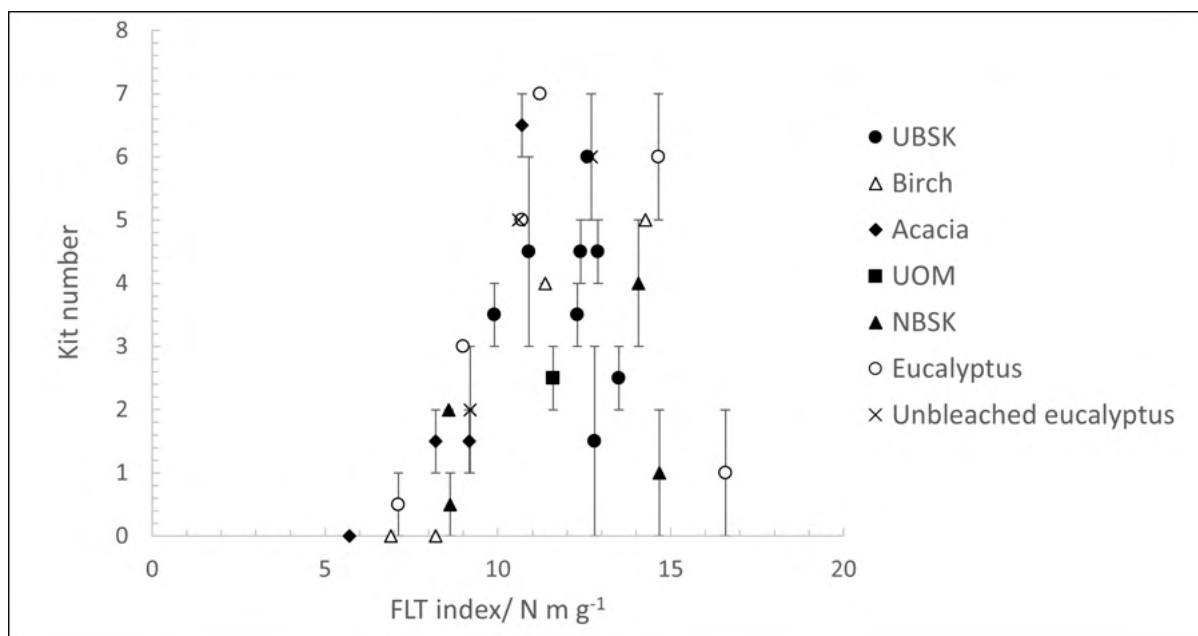


Fig. 7.14. Kit number of sheets coated with 6 g m^{-2} of MFC as a function of the FLT index of the MFC. Kit numbers represent the mid point of two measurements with error bars showing the range of values measured.

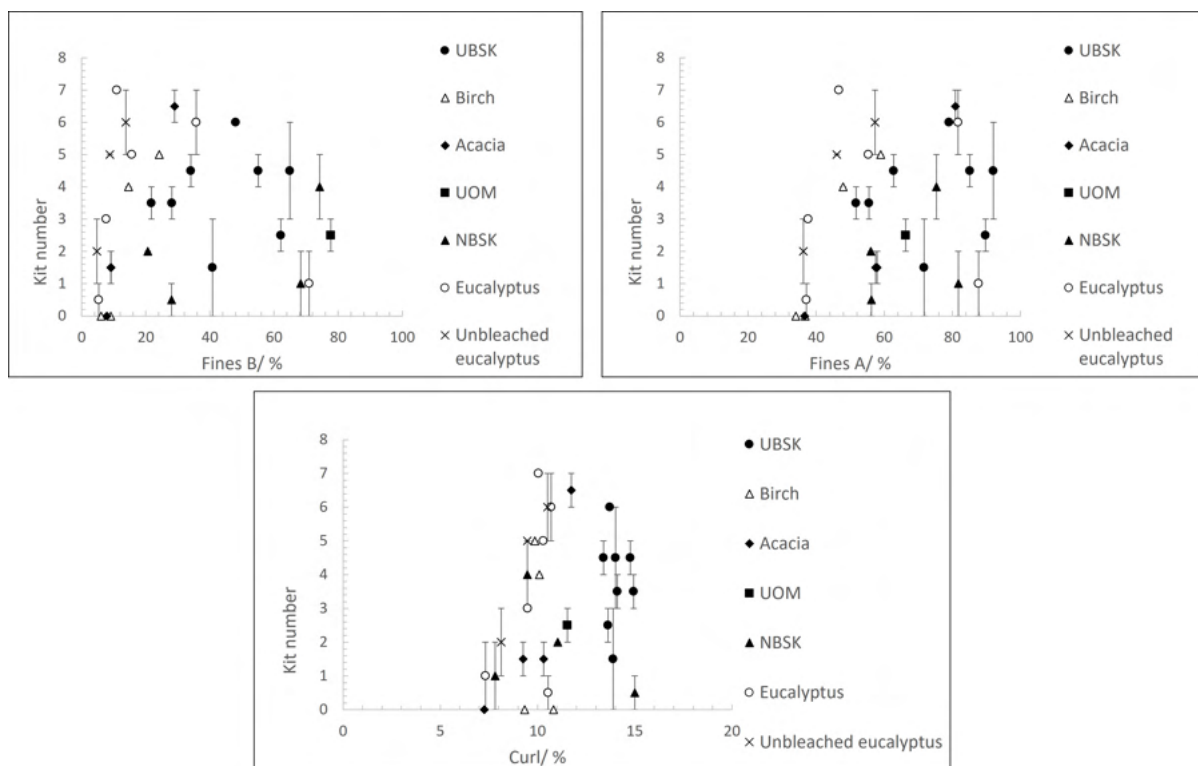


Fig. 7.15. Kit number of sheets coated with 6 g m^{-2} of MFC as a function of fibre image analyser parameters Fines A, Fines B, and Curl. Kit numbers represent the mid point of two measurements on two separate sheets with error bars showing the range of values measured.

average diffusion of molecules of heptane through a larger area, where the impact of a defect might be less than if the grease barrier is only tested on the site of a defect.

Johansson and co-authors found that small holes in barrier coatings- known as pinholes- caused a significant disruption in the oxygen barrier properties. Increasing size of pinholes increased OTR of the material¹⁹⁴. A later study found that OTR through a pinhole in aluminium foil filled with low density polyethylene film was two orders of magnitude higher than the OTR through a low density polyethylene film, suggesting that the rate of gas transport through pinholes is significantly higher than the bulk film.¹⁹⁵ Therefore, pinholes within the MFC coating are likely to have a negative effect on the HVTR as well as the grease resistance. However, the difference between the tests is that the HVTR test covers a larger area and therefore the pinholes will increase the average transmission rate; but in the Kit test, if the oil droplet hits a pinhole then the test immediately fails. Kjellgren argued that greaseproof paper provides a grease barrier because there is a dense layer which is impermeable to oil and grease, therefore creating a physical barrier. In this case, the grease resistance of greaseproof paper fails because of small defects and pinholes.¹⁹⁶ This is likely to also be the case with an MFC layer.

Bendtsen Porosity Relation to Barrier Properties

Figure 7.16 shows the relation between the Bendtsen porosity, HVTR and Kit number of MFC coated sheets. Clearly, there is a correlation between decreasing HVTR and decreasing Bendtsen porosity. This could be because although Bendtsen porosity measures air being forced through a paper structure, the air may be forced through by the same connected pore pathway as heptane vapour would diffuse. The correlation between Kit test and Bendtsen porosity is less clear. This could be because the Kit test is highly sensitive to pinholes and

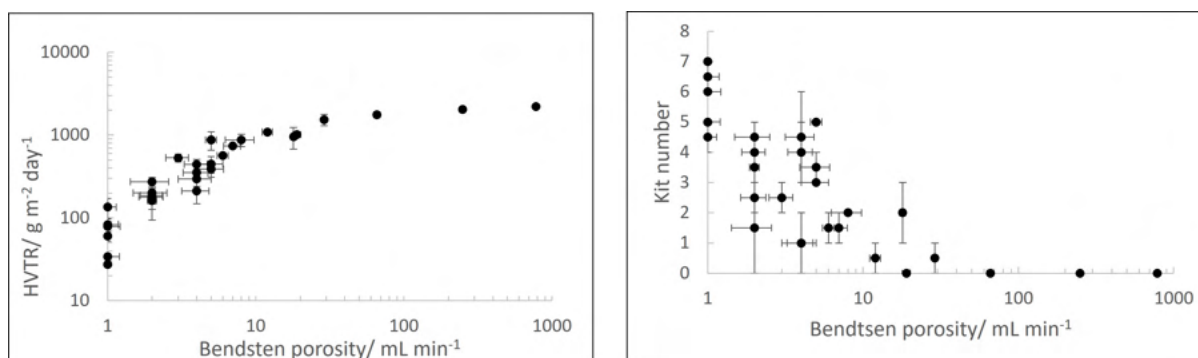


Fig. 7.16. Relation between HVTR and Bendtsen porosity and Kit number and Bendtsen porosity of sheets coated with 6 g m^{-2} of MFC. Kit numbers represent the mid point of two measurements on two separate sheets with error bars showing the range of values measured. HVTR measurements represent the average of three measurements with standard error shown in error bars. Bendtsen porosity values represent the average of five measurements and error bars represent standard error

defects. The Bendtsen porosity test is significantly faster than the HVTR or Kit test and does not require the use of hazardous solvents. It is clear that good barrier properties do not begin to develop until a Bendtsen porosity of below 10 mL min^{-1} has been reached. Therefore, Bendtsen porosity could be a useful screening test in the future to decide which MFC coated paper samples will provide good barrier properties and be taken forward to barrier tests.

Optical Properties of MFC Coatings

Chapter 5 showed that the wavelength exponent of MFC sheets could be related to the grease resistance of MFC coatings. The light scattering coefficient of the MFC coatings made in this thesis chapter were measured over the wavelength of visible light. Figure 7.17 shows the logarithm of the Kubelka-Munk scattering coefficient of an acacia MFC coating layer as a function of the logarithm of the wavelength. Clearly, this is not a linear relationship as was observed for MFC films in Chapter 5. This non linear relationship was seen throughout the MFC coatings.

To further understand the unexpected relationship between Kubelka Munk scattering coefficient and wavelength seen in 7.17, the S and K coefficients were plotted against wavelength for three samples. These samples were: a 6 g m^{-2} MFC coating layer, a corresponding MFC film at 45 g m^{-2} , and the base paper. Results are shown in Figure 7.18. The Kubelka-Munk scattering coefficient S showed a linear decrease with increasing wavelength for the base sheet and MFC film. However, as in Figure 7.17, there is not a linear relationship between S and wavelength for the MFC coating.

The MFC film shows an exponential decrease in K as wavelength increases. However, the base sheet shows a clear peak at 580 nm. This peak can also be seen in the calculated absorption coefficient of the MFC coating. This suggests that the strong absorption of the base paper was affecting the calculated absorption coefficient for the MFC layer. This could be because the MFC layer was relatively thin at only 6 g m^{-2} and therefore did not have a high enough opacity to hide the base sheet. Alternatively, this could suggest that the MFC layer may be irregular, possibly because of the effect of the base sheet, leading to an interface layer where the absorption and scattering coefficient of the base sheet are measured alongside the MFC coating. The Kubelka-Munk approximation assumes that S and K are constant throughout the sample.¹³⁴ Therefore, if there was an interface layer between the MFC coating and the base paper, this would mean that the calculation of S and K would be less accurate. Furthermore, S

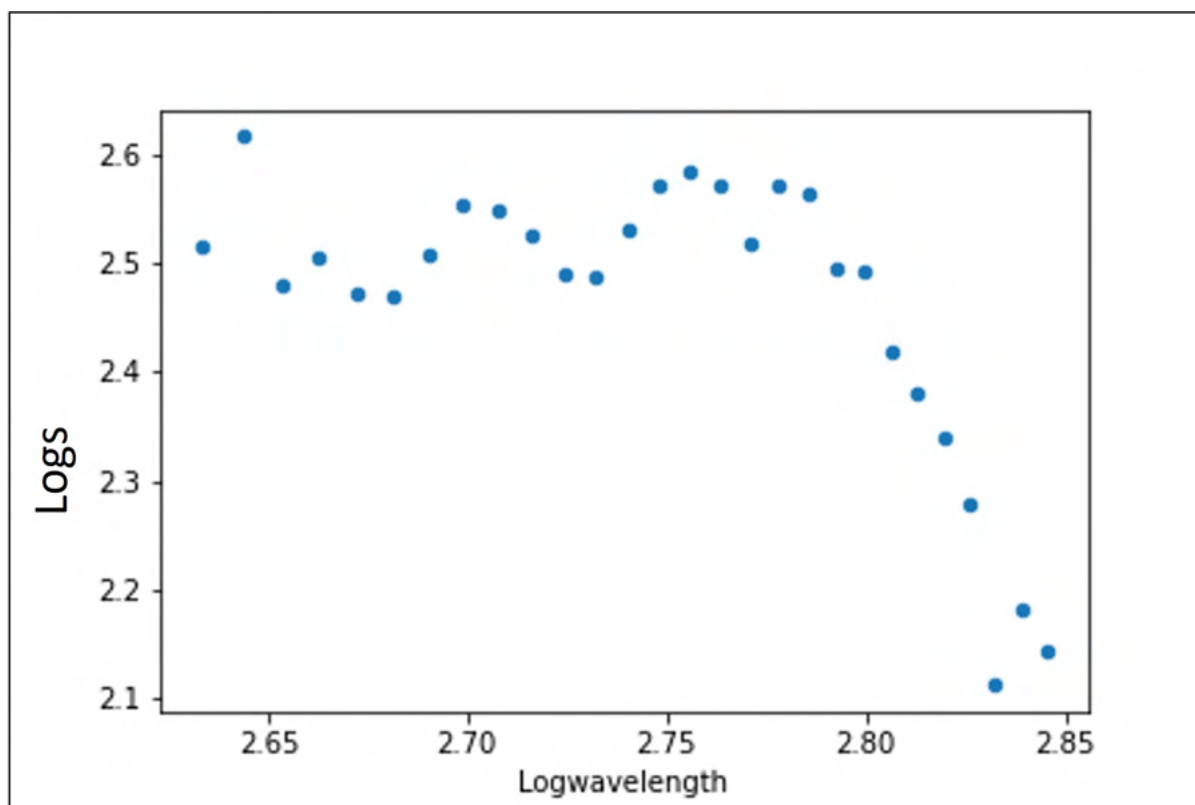


Fig. 7.17. Logarithm of Kubelka- Munk scattering coefficient of a 6 g m^{-2} acacia MFC coating as a function of the logarithm of the wavelength. This represents a wavelength range of 430-700 nm.

and K are not independent of each other.¹⁹⁷ Nordman and co-authors found that if absorption of a sheet is increased in a specific wavelength by adding a dye, then the Kubelka Munk scattering coefficient will decrease in that wavelength range.¹⁹⁸ Endström and co-authors also observed a dependence between Kubelka-Munk scattering and absorption coefficients.¹⁹⁹

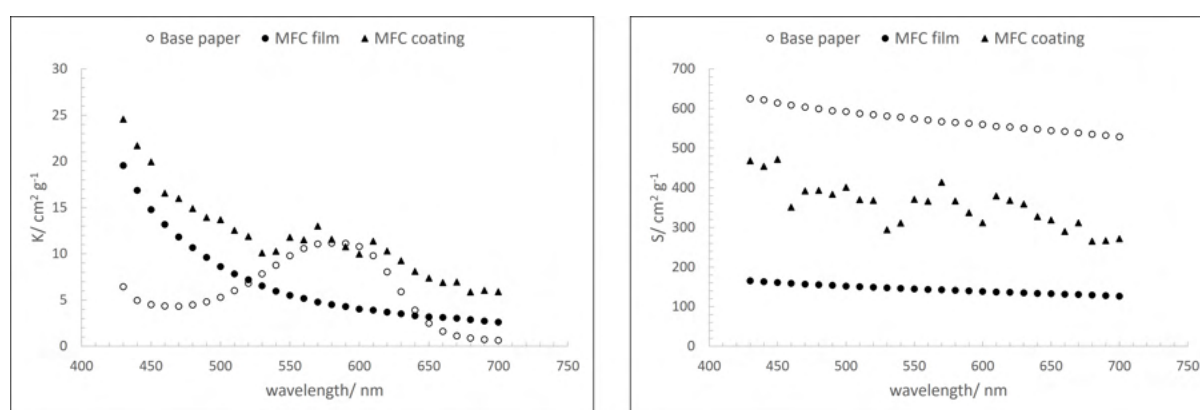


Fig. 7.18. Kubelka Munk S and K of base paper, MFC film and MFC coating as a function of wavelength

7.3.3 Addition of Large Fibres

Fibre image analyser parameters for the disintegrated eucalyptus fibres showed that the length weighted average length ($l_c(l)$) of the large eucalyptus fibres was 0.744 mm and the average

fibre width was $14.07\ \mu\text{m}$. Figure 7.19 shows that the FLT index decreases as the weight percentage of large fibres added into the MFC increases. This is likely because the large fibres added into the MFC have replaced some of the mass of MFC in the mineral-MFC sheet used in the FLT test; leading to an overall reduction in cellulose surface area and therefore a reduction in the entanglement and hydrogen bonding between cellulose surfaces.

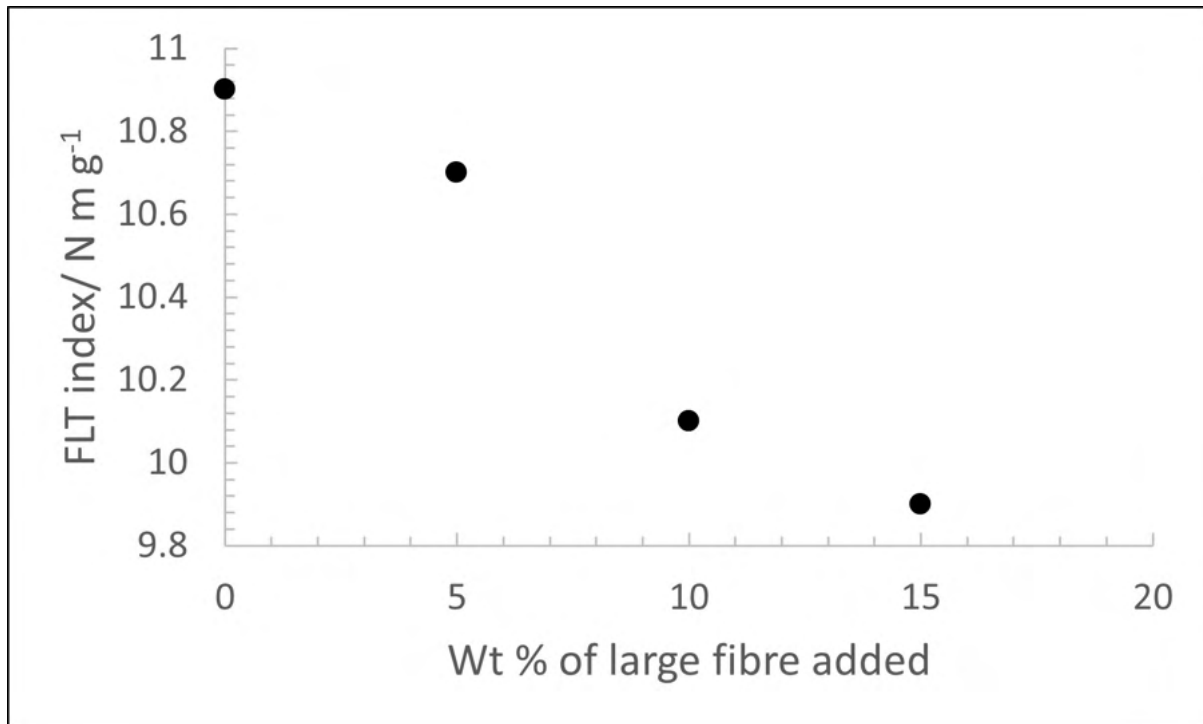


Fig. 7.19. Measured FLT index as a function of the weight percent of large fibres added into the MFC.

Optical microscope images of the large fibres that were added into MFC suspensions are shown in Figure 7.20.



Fig. 7.20. DIC optical microscope images of eucalyptus fibres produced through disintegration of pulp in a 0.08 wt% suspension.

Laser Profilometry of Coated Sheets

Figure 7.21 shows the height profiles of the MFC coated sheets with increasing doses of large fibres. The images show that the large fibres resulted in a disturbance in the height of the coated sheets, since more large fibres are visible as the weight percentage of large fibres increases. This could indicate that large fibres may result in more porosity within the MFC

layer if the height disturbances cause defects in the coatings. However, it could be that the large fibres are embedded within a network of MFC and therefore may not result in increased porosity. The height profile images from the laser profilometer do not provide high enough resolution to determine this. SEM images of the surfaces would be required to make this determination.

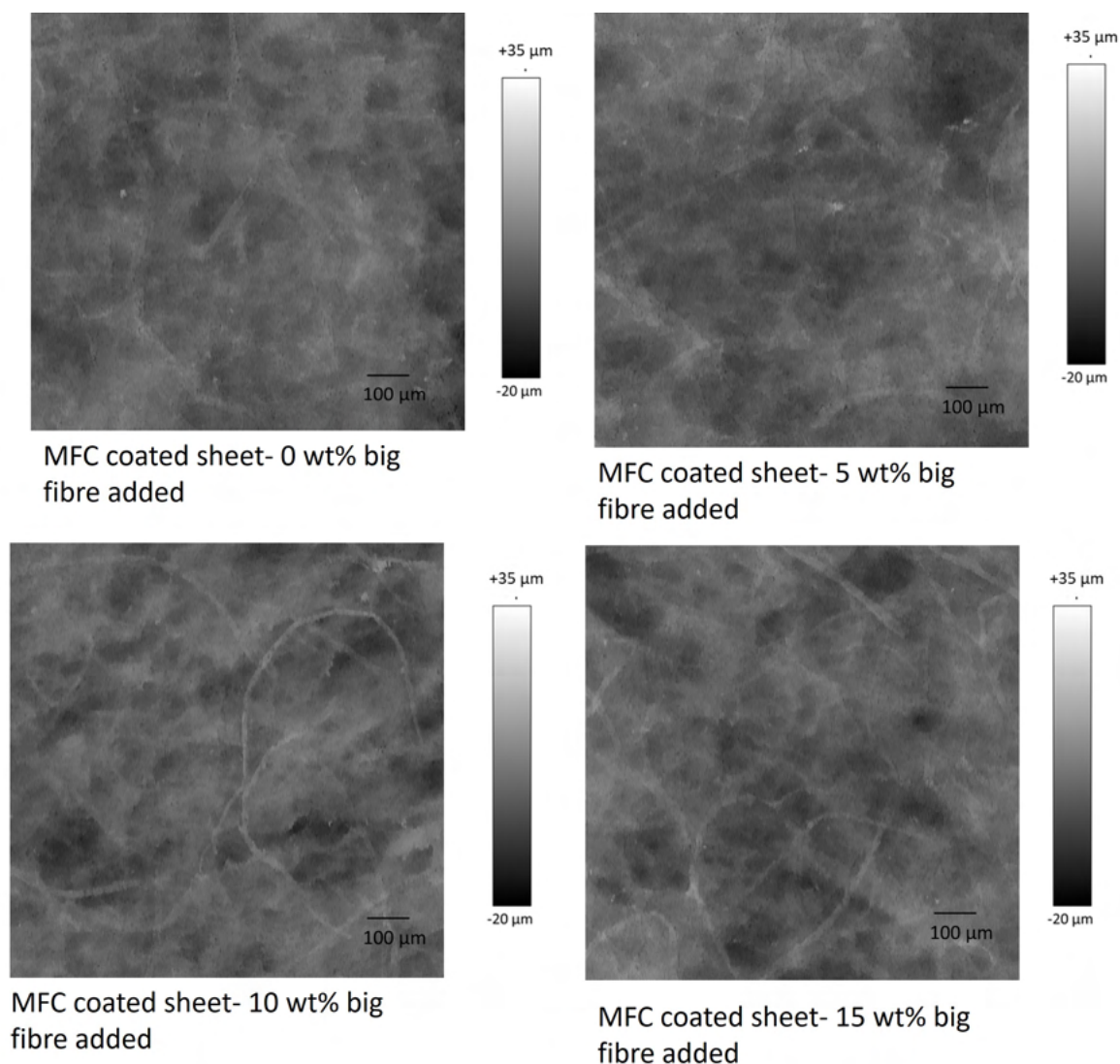


Fig. 7.21. Interferometric laser profilometer Height profiles of 6 g m^{-2} MFC coated sheets with increasing doses of large fibres added into the MFC.

Barrier Properties

Figure 7.22 shows the variation of air permeability, HVTR, and grease resistance when increasing wt% of large eucalyptus fibres are added into the MFC coating. The addition of 5 wt% large fibres appears to make only a small difference to the barrier properties. However, the addition of 10 wt% large fibres causes an increase in air permeability and HVTR and a decrease in grease resistance. This is likely to be due to the large fibres causing some disruption in the MFC layer, leading to increased porosity and allowing the transport of air, heptane vapour and grease through the MFC layer. However, the HVTR of the 10 wt% large fibre coated sheet was $107 \pm 22 \text{ g m}^{-2} \text{ day}^{-1}$ in comparison to $2217 \pm 6 \text{ g m}^{-2} \text{ day}^{-1}$ for the uncoated base

sheet. Therefore, the MFC layer still provided significant barrier properties despite having 10 wt% of MFC replaced with large untreated fibre.

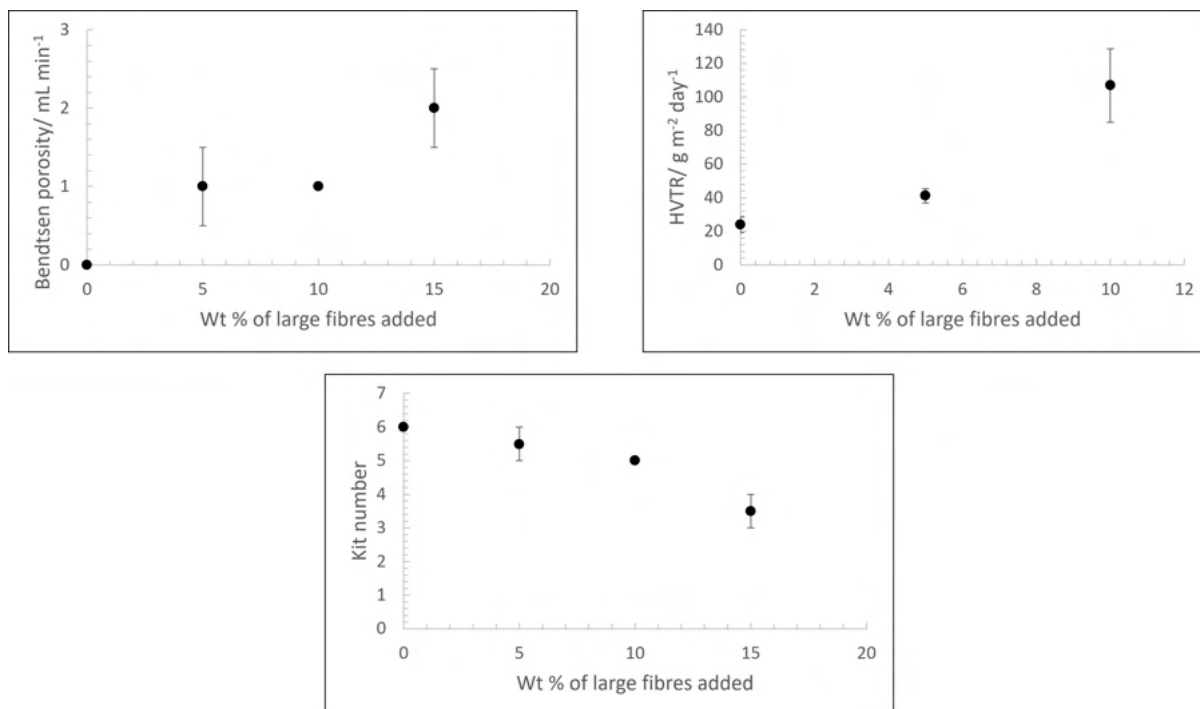


Fig. 7.22. Air permeability, HVTR and Kit number of MFC coated sheets with added large eucalyptus fibres into the MFC.

7.3.4 Multiple Layers of MFC

SEM Images

To understand the structure of the multi layered MFC sheets and how the structure was influenced by the order of application of different MFC samples, SEM images of surfaces and cross sections of eucalyptus MFC coated sheets were taken. Figure 7.23 to Figure 7.26 show these images. The surface of the sheet coated with High followed by Low Fines B eucalyptus MFC shows more roughness and surface irregularity than the sheet coated with Low followed by High Fines B eucalyptus MFC. However, it is difficult to determine from the SEM cross sections if there is any additional penetration of the MFC into the base sheet.

Barrier Properties

Table 7.4 shows the barrier properties of sheets coated with multiple layers of MFC. The sample coated with the high Fines B eucalyptus MFC had the highest Bendtsen porosity and HVTR and the lowest Kit number, in accordance with Figure 7.11, Figure 7.14, and Figure 7.12. However, coating the MFC in two layers significantly improved the barrier properties, even when the high Fines B eucalyptus MFC was applied in two separate layers. This may have been because the water was completely drained out of the MFC suspension for the 2 g m⁻² layer, therefore creating a smoother, lower porosity surface on the paper which allowed a dense layer of MFC to be deposited and meant that more of the fine material remained on the surface. Significantly, it can be seen that applying the low Fines B eucalyptus as a pre-coating before the high Fines B eucalyptus results in lower air permeability, higher grease resistance and lower HVTR. This supports the argument that MFC with a high proportion of

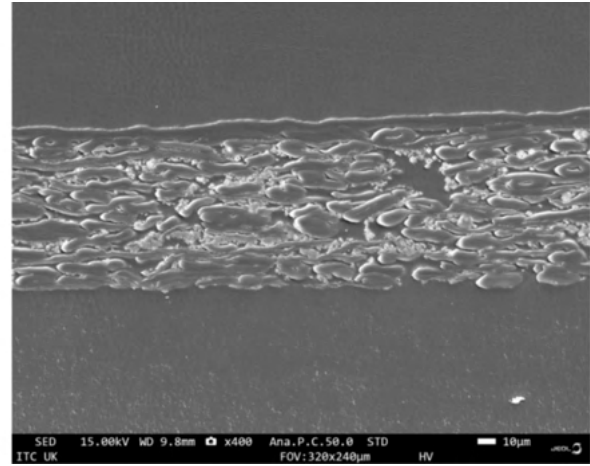
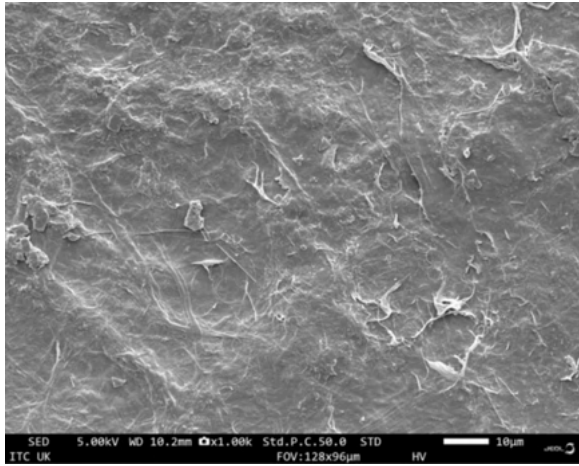


Fig. 7.23. Surface and cross sectional SEM images of base sheet coated with 4 g m^{-2} Low Fines B eucalyptus MFC

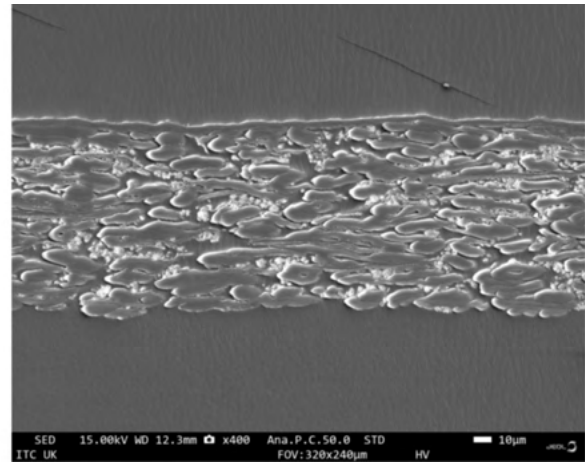
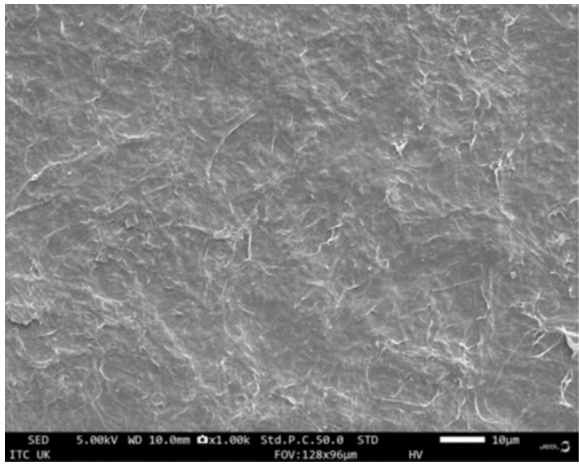


Fig. 7.24. Surface and cross sectional SEM images of base sheet coated with 4 g m^{-2} High Fines B eucalyptus MFC

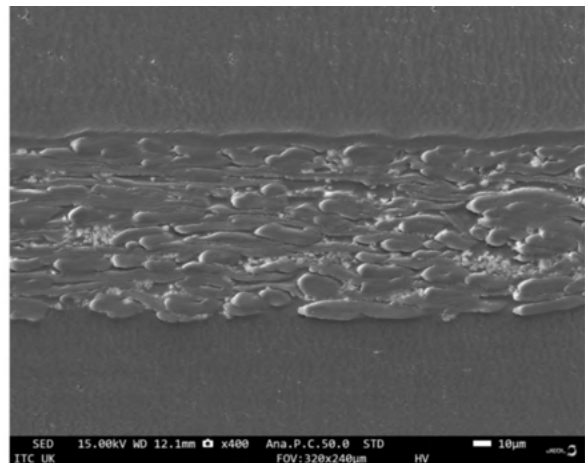
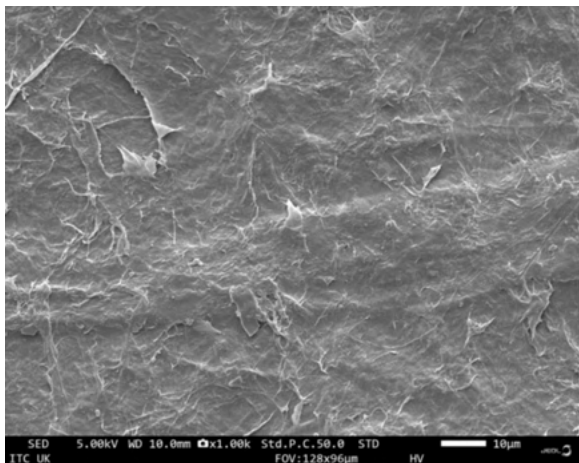


Fig. 7.25. Surface and cross sectional SEM images of base sheet coated with 2 g m^{-2} High Fines B and 2 g m^{-2} low Fines B eucalyptus MFC

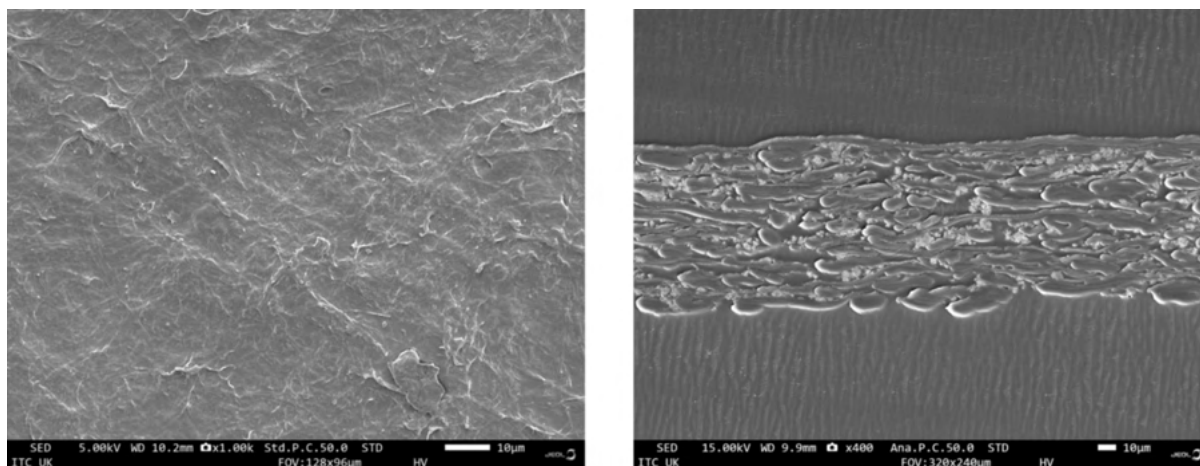


Fig. 7.26. Surface and cross sectional SEM images of base sheet coated with 2 g m^{-2} Low Fines B and 2 g m^{-2} High Fines B eucalyptus MFC

Table 7.4

Air permeability, grease resistance and HVTR of sheets coated with multiple layers of eucalyptus MFC. Errors represent standard error values.

Sample description	Coat weight g m^{-2}	Bendtsen Porosity mL min^{-1}	HVTR $\text{g m}^{-2} \text{ day}^{-1}$	Kit
E1	4	2 ± 0	289 ± 55	2 ± 0.5
E1	$2 + 2$	1 ± 0	130 ± 55	4 ± 0.5
E2	4	13 ± 1	836 ± 67	1 ± 0.5
E2	$2 + 2$	1 ± 0	46 ± 1	4 ± 0
E2 + E1	$2 + 2$	2 ± 0	116 ± 8	4 ± 0.5
E1 + E2	$2 + 2$	1 ± 0	47 ± 3	5 ± 0

fine cellulose material may make less effective barrier coatings on porous paper due to loss of material into the base sheet.

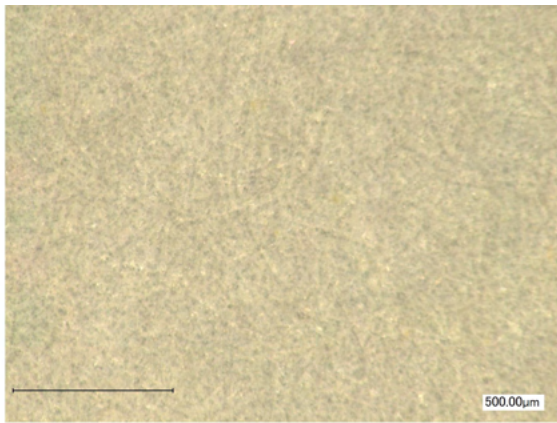
7.3.5 MFC Films

Optical Microscopy

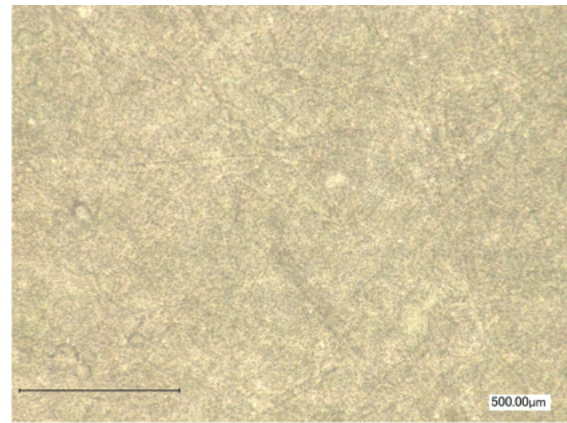
Figure 7.27 shows optical microscope images of MFC films made from selected MFC samples used in coatings earlier in the chapter. The presence of large fibres can be observed in the acacia, birch and lower FLT eucalyptus MFC films. This effect has been observed previously in Chapter 5 and Chapter 6.

Optical Properties

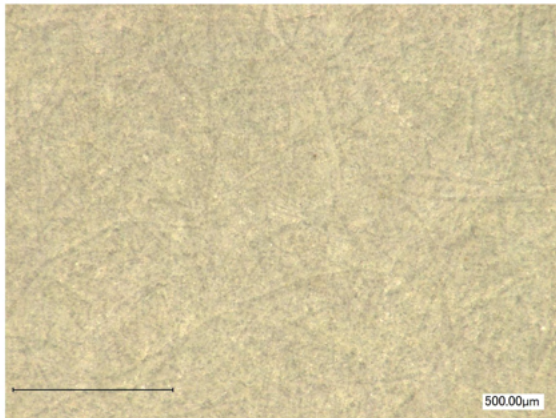
Figure 7.28 shows the optical properties of the MFC films. There is an overall increase in wavelength exponent of the MFC films as the FLT index increases, which was also observed in Chapter 5. This was an expected result because more highly dispersed fibrils should form a cellulose film with smaller pores, as observed in the wavelength exponent data in Chapter 5 where the wavelength exponent increased with increasing Fines A, Fines B and FLT index. However, there was no correlation between S and FLT index, possibly due to competing effects of increasing fibrillation decreasing light scattering due to a lower unbonded surface area of cellulose and increasing fibrillation leading to smaller pore size which resulted in stronger light scattering.¹³⁶



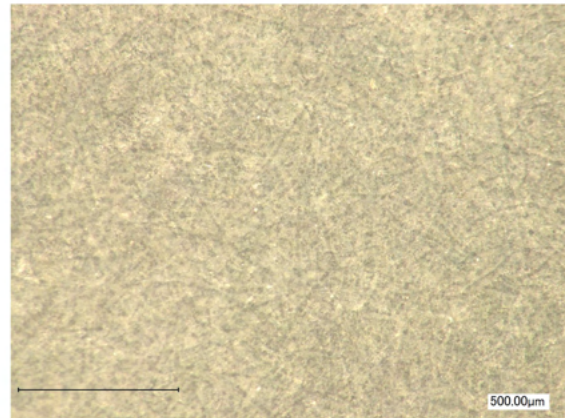
Acacia, FLT 8.2 N m g⁻¹



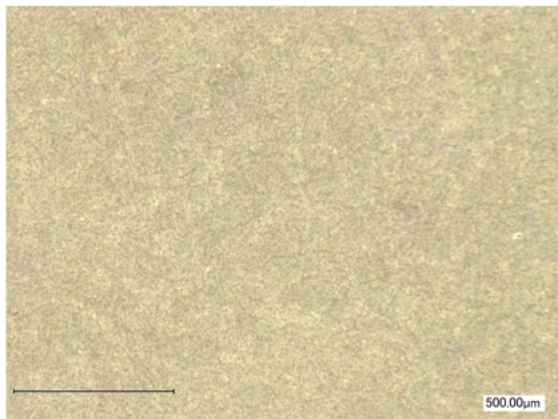
Birch, FLT 14.3 N m g⁻¹



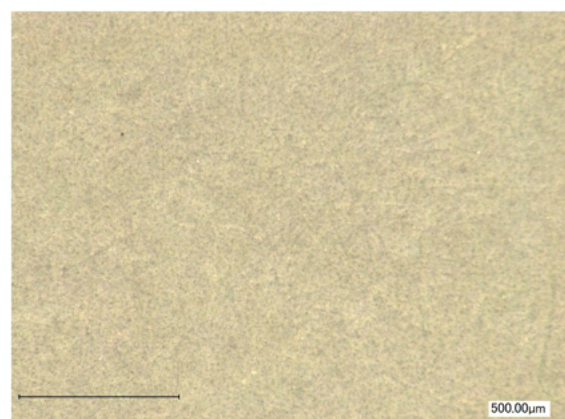
Eucalyptus, FLT 10.7 N m g⁻¹



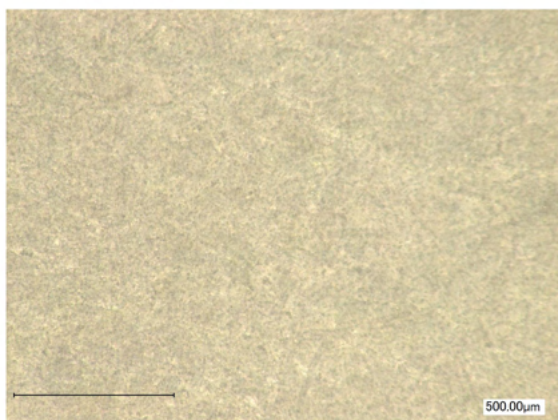
Eucalyptus, FLT 7.1 N m g⁻¹



Eucalyptus, FLT 14.6 N m g⁻¹



Eucalyptus, FLT 16.6 N m g⁻¹



University of Maine, FLT 11.6 N m g⁻¹

Fig. 7.27. Optical microscope images of MFC films captured using a Keyence digital microscope.

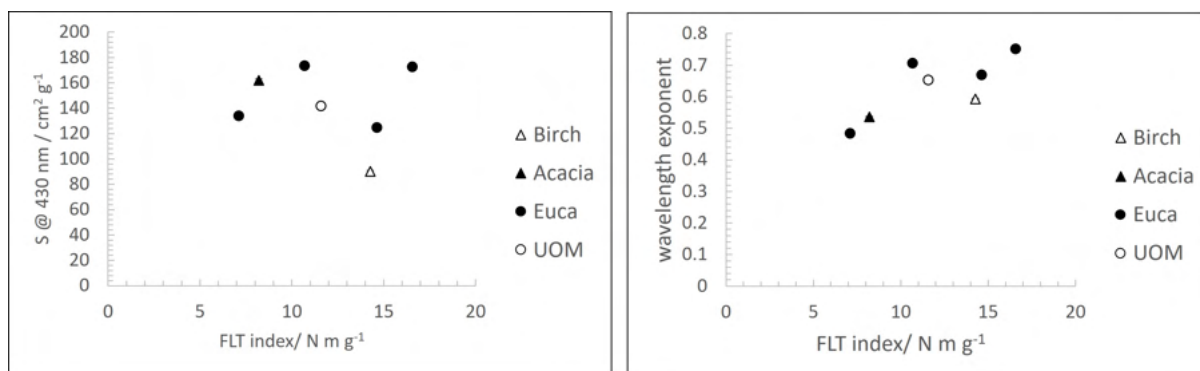


Fig. 7.28. Optical properties of MFC films, including scattering coefficient at 430 nm and wavelength exponent

Density

Figure 7.29 shows how the density of MFC films, measured through digital micrometer, varied with increasing FLT index, Fines A, and Fines B. There was an overall increase in density with increasing FLT index and Fines A. This is similar to the relationship between density of MFC films, FLT index, and Fines A seen in Chapter 5. There is less of a clear relationship with Fines B in the current chapter but this may be because there were fewer MFC samples.

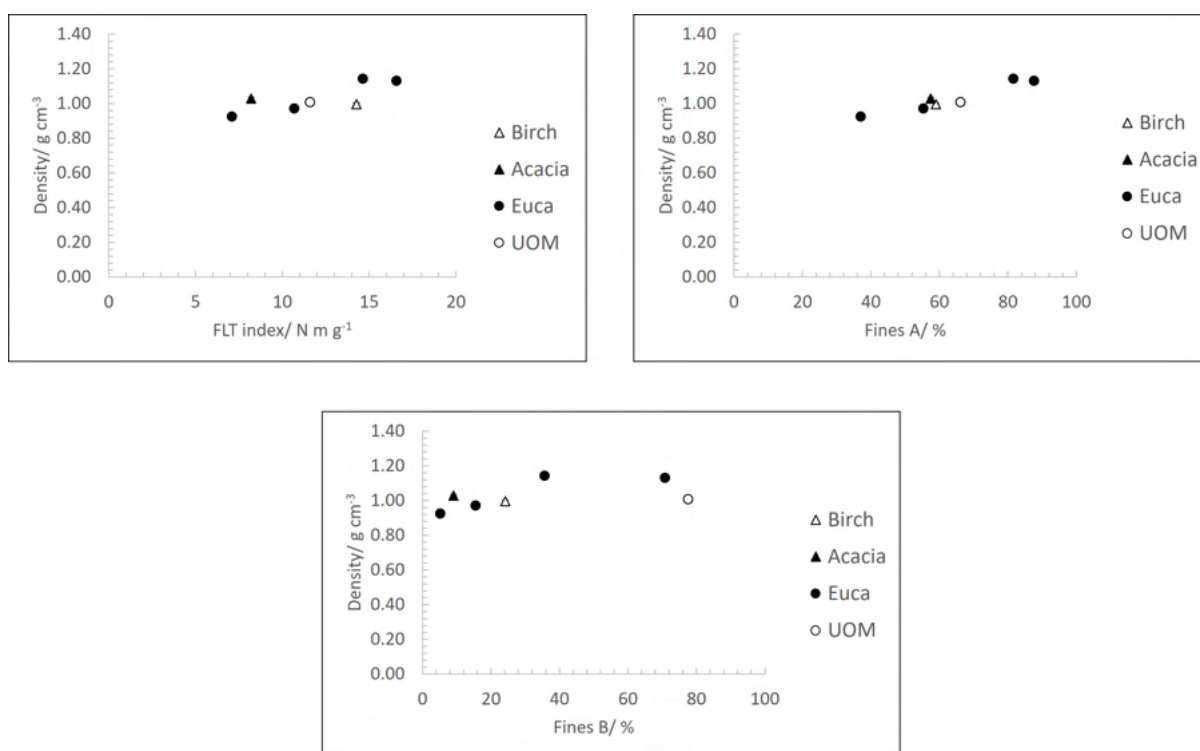


Fig. 7.29. Density of MFC films measured using a digital micrometer

Porosimetry

Improvement of Porosimetry Measurements

In Chapter 6, porosimetry was performed by folding MFC films into concertina shapes in order to fit into the glass dilatometer. However, there was significant noise in the data at pore sizes above $10 \mu\text{m}$ as seen in 6.14. Ridgway and Gane suggested that rolling strips of paper was an

effective way to measure pore size distribution.²⁰⁰ Therefore, rolling strips was attempted as an alternative method to attempt to reduce noise.

Figure 7.30 shows the pore size distribution of eucalyptus MFC films measured through either folding or rolling the MFC film to fit into the dilatometer. Rolling the samples to fit in the dilatometer resulted in less noise above 10 μm pore size. This may have been because folding the film sample repeatedly may have led to cracks forming in the surface of the film which may cause noise at higher pore sizes. Since rolling the films produced a cleaner pore size distribution, rolling was used as the method to compare a more and less fibrillated MFC sample.

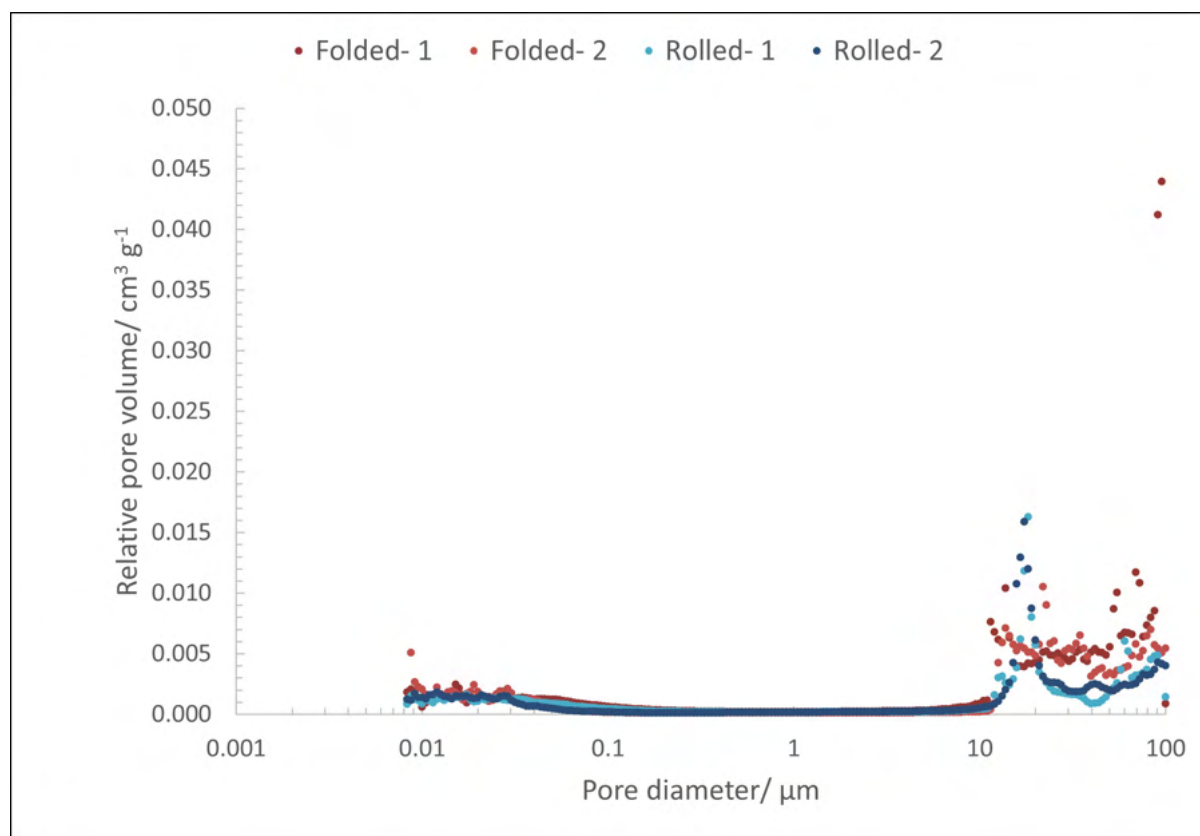


Fig. 7.30. Porosimetry of eucalyptus MFC films. Porosimetry was performed on two films separate film samples for each MFC sample. Films were measured through either folding the sample into a concertina shape to fit into the dilatometer or rolling the film to fit into the dilatometer

Effect of Increasing Fibrillation on Pore Size Distribution

Figure 7.31 shows the pore size distribution of less and more fibrillated eucalyptus MFC films. These are distinguished by high and low Fines A, as provided in the figure caption. The lower Fines A eucalyptus sample showed significantly higher pore volume in the range of 5-40 μm . There is little difference in the pore size distribution of the two MFC samples below 0.1 μm . This implies that pore volume differences between more and less fibrillated MFC samples in films may occur at large pore sizes, possibly due to surface defects from large fibres. It may be that small fine fragments in highly fibrillated MFC fill in gaps between large fibres which leads to a lower pore volume at high pore diameters. Padberg and co-authors found that increasing Fines A of MFC produced through increasing passes through a Supermasscolloider grinder resulted in decreasing cumulative pore volume measured through mercury intrusion

porosimetry.⁵⁸ This agrees with Figure 7.31 shows that the more fibrillated, or higher Fines A, MFC sample produced films with a lower cumulative pore volume.

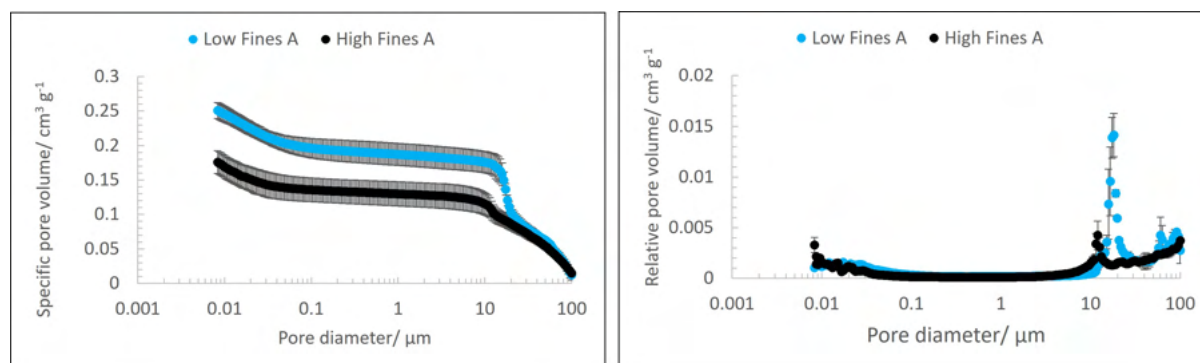


Fig. 7.31. Porosimetry of eucalyptus MFC films. Low Fines A = 37%, high Fines A = 82%. Porosimetry was performed on two separate film samples for each MFC sample, mid points are plotted for each sample and error bars represent range of measurements.

Moisture Content and Water Contact Angle

Figure 7.32 showed only small differences in moisture content at 50% RH and 23°C for the different MFC samples.

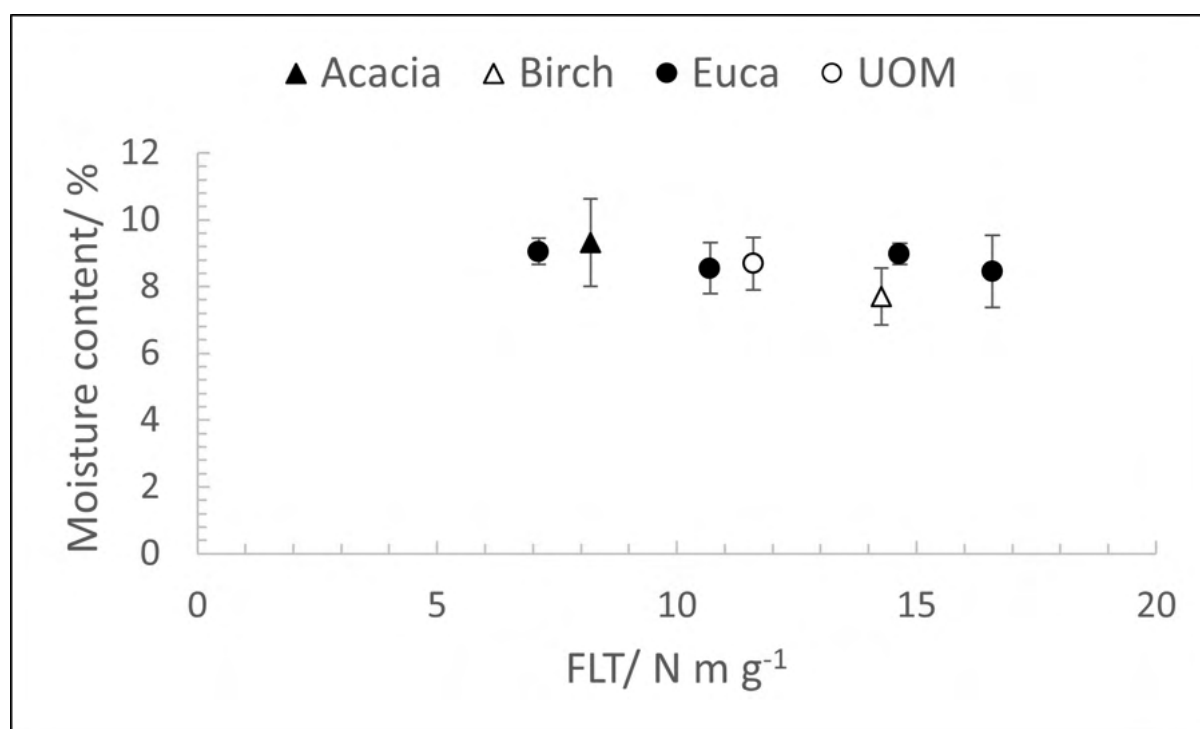


Fig. 7.32. Moisture content of MFC films measured at 23°C and 50% RH

Figure 7.33 shows the water contact angle of MFC films recorded over the space of 60 seconds. Differences in the water contact angle between the films are likely to be due both differences in chemical properties of the pulps and differences in the surface pore structure. For example, Euca FLT 7.1 corresponds to Low Fines A eucalyptus used in the porosimetry experiments and Euca FLT 14.6 corresponds to High Fines A eucalyptus used in the porosimetry experiments. There is a higher water contact angle for the Euca FLT 14.6 despite the pulp types being the

same, therefore further suggesting differences in surface porosity of the film, as observed in the porosimetry data. In the present work, water contact angles for MFC films varied between 52 and 84°. In contrast, MFC films and coatings produced by Rodionova and co-authors varied between 35 and 60°. ²⁰¹ Solala and co-authors found that an NFC film had a contact angle of 25°. ²⁰² Therefore, water contact angles measured in the present work appear to be unusually high. This could be partly because the films in the present work were dried under vacuum pressure at 93°C, which may have led to a denser surface than that of Rodionova and co-authors and Solala and co-authors, and therefore possibly a higher initial measurement of water contact angle. ^{201,202}

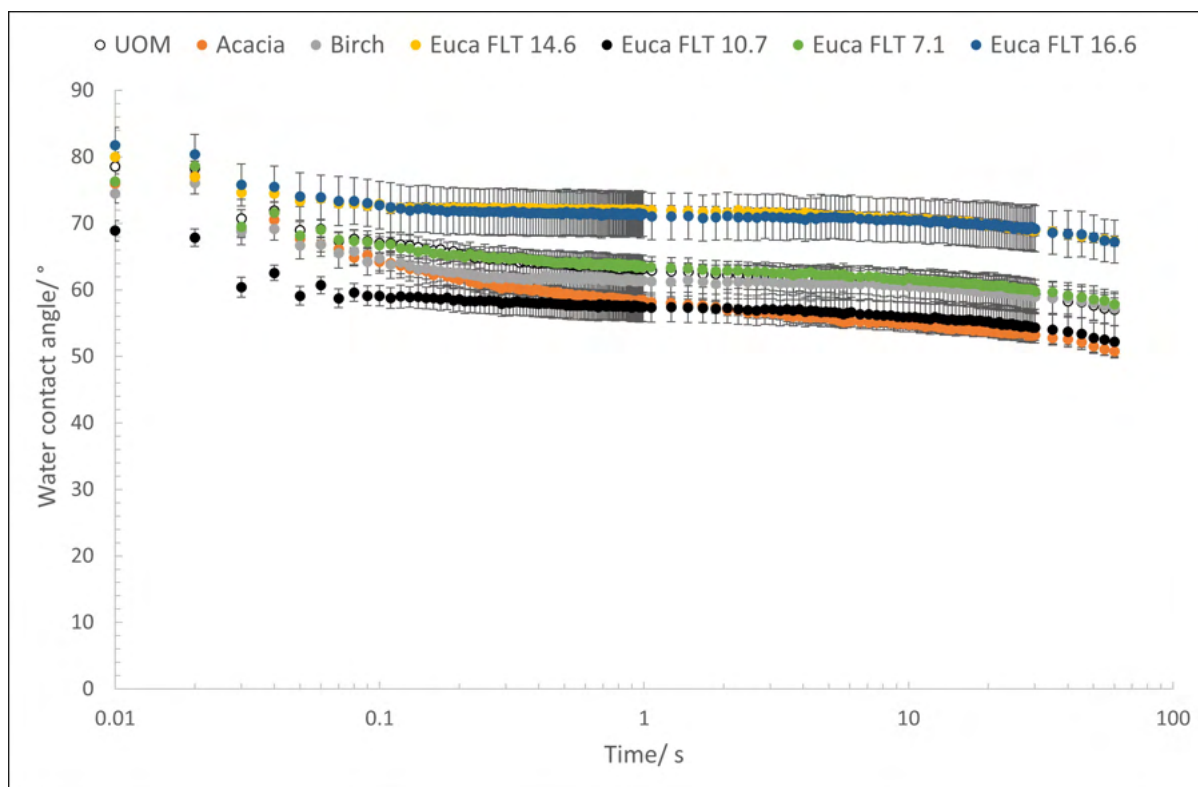


Fig. 7.33. Water contact angle of MFC films measured at 23°C and 50% RH

Water Vapour Barrier

Figure 7.34 shows how the WVTR of MFC films varies with FLT index, Fines A, and Fines B. In this case, it appears that the pulp type has more of an effect on the WVTR than any other parameter. In Chapter 5, it was apparent that increasing the cellulose fibrillation decreased WVTR of MFC films but only up to the point where dense MFC films were formed and then there was no further improvement. It may be that the MFC samples used in the present study were sufficiently fibrillated that they were in this plateau region and increasing fibrillation did not have an effect. In Chapter 5, there was a significant range in density of cellulose films from 0.54 - 1.31 g cm⁻³. However, in the present chapter, the range of density is between 0.92 - 1.14 g cm⁻³ which is a much narrower range in density and may explain why there was not a significant variation in WVTR with increasing fibrillation.

Oxygen Barrier

Figure 7.35 shows the effect of FLT index, Fines A and Fines B on the OTR of MFC films. The data shows only small variation in OTR with changes in cellulose morphology in comparison with variation within the HVTR results. This may be because the OTR test were performed

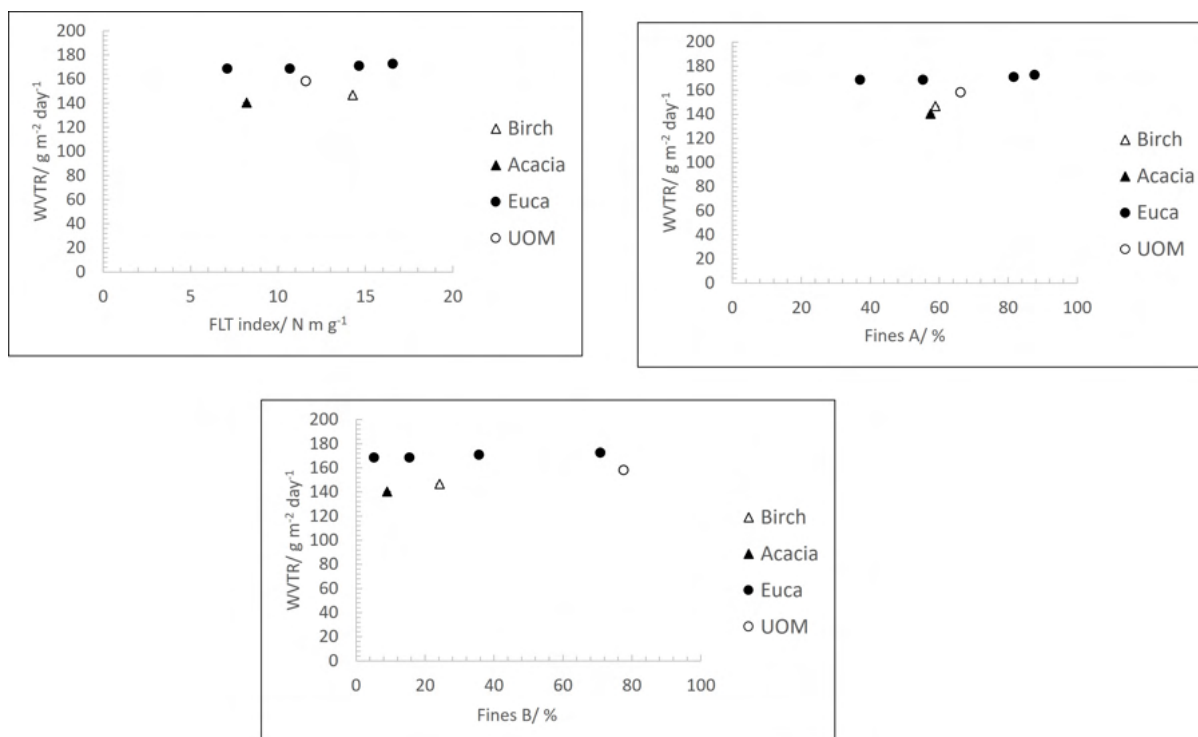


Fig. 7.34. WVTR of MFC films as a function of Fines A and Fines B.

on relatively thick MFC films where the chance of a defect extending throughout the film was low. This may have meant that fibrillation had less effect on barrier properties for thick films than thin coating layers.

Rodionova and co-authors found that MFC films made from bleached spruce pulp had lower OTR for equivalent mechanical and chemical treatments on the cellulose compared to eucalyptus pulp.¹⁰¹ In the present study, the pulp type appears to have more effect on the OTR than differences in fibrillation of pulp. However, this is not likely to be due to differences in moisture sorption between pulp types since the moisture content was shown to be similar for the different samples in Figure 7.32. Bessonoff and Paltakari found that for a 20 g m⁻² MFC film, there was a decrease in measured OTR as the number of passes through a Supermasscolloider increased from 4 to 9 for making the cellulose. However, at a film grammage of 60 g m⁻², there was very little difference between the samples.⁸¹ This is similar to results found in the present research project where the effect of fibrillation on gas barrier properties is large for thin paper coatings but small for thick films.

7.4 | Discussion

The results from the 6 g m⁻² MFC coatings showed that increasing the fibrillation of the MFC, which was measured through the FLT index, decreased the air permeability and HVTR and increased the grease resistance. However, when the fibrillation of the MFC further increased, this led to an increase in HVTR and a decrease in grease resistance. This effect was most notably observed for the bleached eucalyptus pulp samples where there was large increase in Fines B after homogenisation and a decrease in barrier properties. When the HVTR of the MFC samples was plotted against the Fines B of the MFC in Figure 7.13, this suggested that there may be a relation between increasing Fines B and increasing HVTR at high levels of Fines B. This suggests that a decrease in barrier properties of MFC coatings may be due to fine, liberated MFC fibrils falling into the porous base sheet and not retaining on the surface

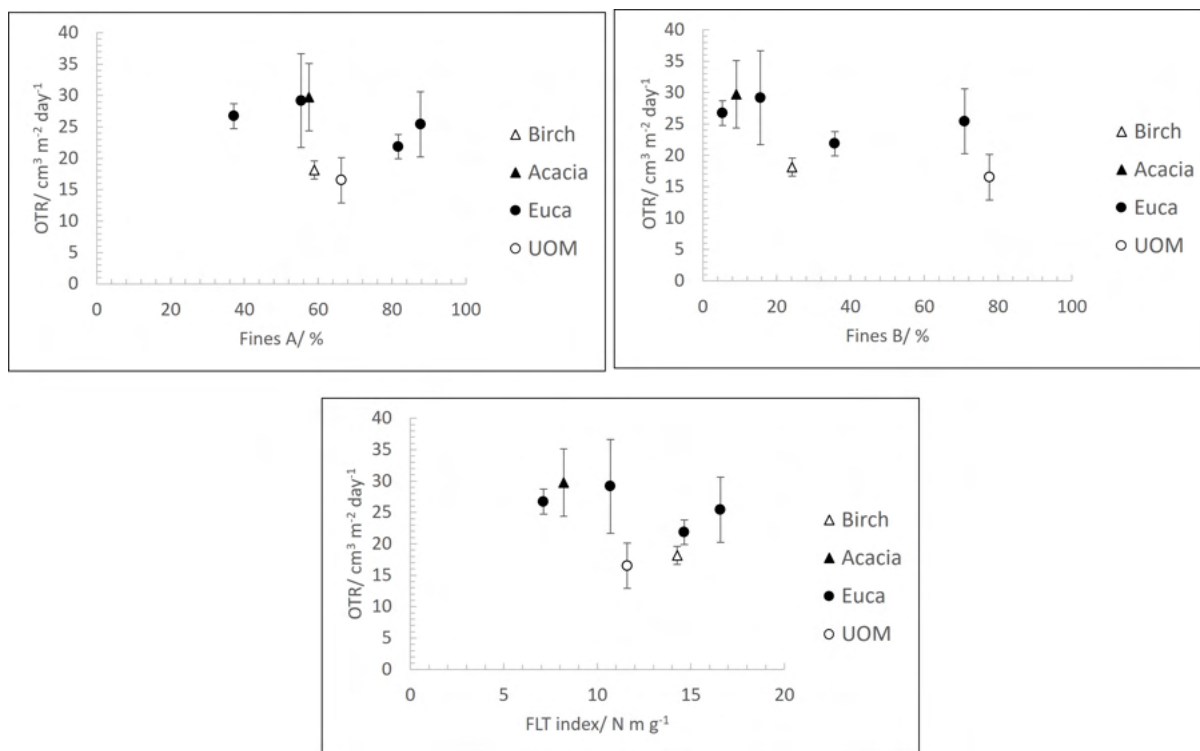


Fig. 7.35. OTR of MFC films as a function of FLT index, Fines A and Fines B.

of the sheet. Material that is made up of coarser aggregates of MFC may be more likely to retain on the surface of the sheet and therefore form a dense film with low porosity.

To test the theory of loss of fine cellulose into the base sheet, multiple layers of MFC were coated. Coating a coarser MFC sample as a pre-coat to a finer MFC sample resulted in improved barrier properties compared to coating the finer MFC as a pre-coat to the coarser MFC. This provides evidence for the theory that using an MFC sample comprised of mostly fine, liberated fibrils, may be detrimental to barrier properties when applied through a filtration mechanism onto a porous base, because some of the fine material is likely to be lost into the base sheet.

When large fibres were deliberately added into the MFC, there was a decrease in barrier properties, but the effect was relatively small, indicating that some large residual fibres remaining in the cellulose after processing may not have a strong negative effect on barrier properties. Additionally, the addition of large fibres also resulted in a decrease in the FLT index of the material. This means that the presence of large fibre fragments in MFC should not have affected the relationship between FLT and barrier properties that was observed in Chapter 4. Therefore, although this may be a contributing factor, it does not explain why the NBSK MFC sample in Chapter 5 showed poor barrier properties in relation to the eucalyptus sample. This is more likely to be because the NBSK sample was homogenised and had a high Fines B measurement (73%) compared to the eucalyptus sample (17%), and therefore less of the NBSK MFC was retained on the sheet surface in comparison with the eucalyptus MFC. When MFC films were made, porosimetry measurements showed a reduction in pore volume of eucalyptus MFC films with a higher level of fibrillation. However, there were only small differences in WVTR and OTR between samples. This suggests that the barrier properties of thin coatings is likely to be more affected by changes in the morphology of the cellulose than thick layers of MFC, probably because there is a greater chance of a defect in a thin film leading to connecting porosity throughout the MFC layer. Differences in the pore volume between less and more fibrillated eucalyptus films but little difference in the oxygen barrier

properties suggest that this pore volume may consist of surface porosity which does not extend throughout the MFC film. Therefore, measurement of the structure and barrier properties of thick MFC films does not necessarily correlate with the structure and barrier properties of MFC coatings.

Chapter 5 showed that the light scattering properties of MFC films showed a strong relation with the barrier properties of MFC coatings. In the present chapter, the light scattering of the MFC coatings were measured to investigate whether this could be used as a rapid screening tool to find MFC coatings that may have effective barrier properties. However, there were non linear relationships between scattering coefficient and wavelength, which suggests that the Kubelka-Munk approximation may not have been valid. This may have been because there were not two independent layers of base sheet and coating, but in fact an interface layer, which led to interference from the base sheet optical properties in calculation of the MFC light scattering properties.

7.5 | Conclusions

The present thesis chapter shows that effective MFC barrier coatings can be produced from multiple different pulp types. Furthermore, MFC characterisation techniques such as measurement of the FLT index, Fines B, and Fines A can be helpful tools to understand whether or not an MFC sample is likely to form an effective barrier layer. The present chapter also showed that obtaining an MFC sample with a high enough surface area to form a dense network with low porosity, but also with coarse enough aggregates and particles that it can retain on the surface of the sheet is key to selecting an MFC sample with optimum barrier properties. The issue of loss of fine MFC into the sheet may be mitigated by applying a pre-coating layer of coarser MFC.

Conclusions and Future Work

Selecting the Coating Method for Application of Microfibrillated Cellulose

Coating microfibrillated cellulose onto a porous paper substrate using vacuum filtration was shown to be an effective way to improve the barrier properties of the paper to grease and oil vapour. Two methods of coating cellulose were compared, one where a fresh laboratory made sheet was coated and one where a commercial paper substrate was re-wetted and coated. In both cases, increasing the coat weight of MFC on the paper surface improved the barrier properties. The method of applying the MFC to the re-wetted commercial substrate was selected for the remainder of the project because the base would be consistent without the need to make up multiple batches of pulp.

Increasing Fibrillation of NBSK Fibres Improved Barrier Properties of MFC Coatings

Laboratory refining of NBSK cellulose pulp was effective in decreasing the air permeability of base sheets coated with 10 g m^{-2} of the refined pulp samples. However, even the highest level of laboratory refining, producing a pulp with 65 CSF, did not provide barrier properties to oil and was much less effective than MFC in forming a barrier to heptane vapour. MFC produced through grinding formed coatings with effective barriers to grease and heptane vapour. However, these barrier properties were further improved by adding a homogenisation step to the MFC. This change could be correlated with a large increase in the proportion of Fines B or high aspect ratio fines in the cellulose material after homogenising.

Films of the refined pulp or MFC showed that increasing the fibrillation of cellulose from fibres to MFC significantly decreased the water vapour transmission rate. However, further increasing the degree of fibrillation through increasing grinding energy or homogenisation pressure did not further improve the water vapour transmission rate, possibly because a film with low porosity had already formed and water vapour was travelling through the cellulose rather than through pores. A small decrease in cellulose crystallinity was measured for homogenised and high grinding energy samples compared to the untreated cellulose. However, this decrease in crystallinity did not appear to have any significant negative effect on barrier properties. This implies that increasing the fibrillation of the cellulose and therefore altering the physical structure of the MFC coating has a greater effect on the barrier properties than small changes in cellulose crystallinity.

Tensile and Optical Properties as Potential Screening Tests for Barrier Properties

Results from the series of increasing fibrillation of NBSK pulp from fibres to fine MFC suggested that a Fiberlean Technologies quality control measure of the tensile strength index of sheets made from 20 wt% MFC and 80 wt% mineral correlated with improved heptane vapour and grease barrier properties of MFC coatings. Therefore, this measure could possibly be used to screen samples which may form effective barrier layers and therefore reduce the number of time

consuming barrier tests required. This topic was further investigated in Chapters 6 and 7. In addition, the Kubelka-Munk Scattering coefficient of cellulose films was used to calculate the wavelength exponent of the films, a parameter related to size of the scattering particles. The wavelength exponent of the MFC films was shown to correlate with grease barrier properties of the MFC coatings. The required optical testing is significantly less time consuming than barrier testing and requires no use of hazardous solvents. Therefore, optical analysis of MFC films could be a useful way to screen samples which may be effective barrier layers.

Coat Weight and Fibrillation are both Important for Barrier Properties

When comparing MFC samples with different levels of fibrillation at increasing coat weights, it was observed that increasing coat weight may be used to compensate for the use of an MFC material with a lower level of fibrillation. This could be useful in an industrial coating situation if the MFC sample must be made with lower energy.

However, this part of the research project showed that an apparently coarser eucalyptus MFC sample had superior barrier properties when coated onto the base paper compared to a homogenised NBSK MFC sample used in the previous chapter. The eucalyptus MFC had a lower proportion of high and low aspect ratio fines than the homogenised NBSK sample, however there was a lower proportion of large fibre fragments in the eucalyptus MFC. Films of the MFC samples showed that the eucalyptus MFC films were less dense than films of homogenised NBSK MFC despite having superior barrier properties when coated onto paper in thin layers. This could have been because the large fibre fragments present in the NBSK MFC may have caused less disruption in a thick film rather than a thin coating layer. However, there could also have been an effect of pulp type on barrier properties of MFC.

Pulp Type has a Substantial Impact on the Effect of Fibrillation on Barrier Properties

The effect of pulp type and fibrillation on barrier properties was studied in the final research chapter by comparing MFC coatings across a range of pulp types and fibrillation levels. Results showed that in general the FLT index correlated with improved barrier properties for MFC coatings. However, for eucalyptus MFC there was a clear increase in HVTR and decrease in grease resistance for a homogenised MFC sample compared to a lower FLT, lower Fines B, non-homogenised sample. This suggested that possibly MFC samples with a high proportion of fine material may not form as effective barrier coatings due to loss of fine material into the porous base sheet, resulting in less MFC on the surface to form a dense film. This argument was supported by coating a thin layer of coarser MFC as a pre-coat to the finer MFC and observing improved barrier properties compared to coating the finer MFC as a pre-coat to the coarser MFC. There was less effect of fibrillation on barrier properties of thick films of the MFC than for thinner MFC coatings. This could have been because the probability of a defect extending throughout a thick MFC film allowing diffusion of gas is smaller than for a thin MFC coating.

Industrial Relevance of the Findings

This research project showed that Fiberlean MFC can form effective barrier layers when coated onto paper surfaces through vacuum filtration and that the level of fibrillation of the MFC is important to the final barrier properties. The effectiveness of an MFC sample as a barrier layer can be estimated by measuring the tensile strength index of a 20 wt% MFC, 80 wt% mineral sheet. This is a quality control measure performed at Fiberlean Technologies and is a significantly faster test than making MFC coated sheets and measuring the barrier properties.

This would allow MFC samples to be screened to select ones that are likely to be more effective. This measurement could be used in combination with the Fibre Image Analyser parameters, particularly the Fines B and Fines B measurements, to predict which MFC samples may form useful barrier coatings. In addition, studying the optical properties of MFC films may be a useful method to screen which samples are likely to make good barrier coatings. Therefore, the research project has helped to determine which MFC samples should be used in industrial wet end coating applications and helped to provide a useful solution for industrial application of MFC coatings.

Limitations of the Research

Sheets made in this study are formed through vacuum filtration from a highly diluted MFC suspension. Therefore, these sheets represent an MFC layer with ideal formation. In reality, when MFC is coated on an industrial scale, the coated layer is likely to have significantly more defects and pinholes. These defects and pinholes will negatively affect the barrier properties. Therefore, this research shows a method to select an MFC sample which shows the most promise to produce the best barrier properties but does not aid in creating uniform MFC coatings on an industrial scale. The quality of a large scale industrial coating is likely to be lower than that of a sheet made in the laboratory and therefore characteristics of the cellulose may have less effect than issues such as defects and pinholes in the coating when more of these are present. Furthermore, MFC coatings are highly sensitive to moisture and become less effective barrier layers at high humidity levels. This research does not address the issue of moisture sensitivity in the MFC film, and it is assumed that the trend in relations between fibrillation and barrier properties will remain the same at high relative humidity.

Future Work

Future work on this project could involve looking into the effect of the structure of the base sheet on the barrier properties of MFC coatings. For example, laboratory made base sheets could be produced where the cellulose has been refined to different levels, resulting in base sheets with different pore structures. Layers of a less and more fibrillated MFC sample could then be coated onto the base sheets. This would provide further evidence that the structure of the base sheet is important to the barrier properties of the MFC layer. It may be possible to further improve barrier properties by decreasing the porosity of the base sheet through refining, therefore allowing an MFC with a high proportion of fine material to be effectively retained on the surface of the sheet and form a dense coating layer with excellent barrier properties. However, this may result in very slow drainage of the coating since the base sheet will be less porous. Improving the drainage of the MFC suspension through the base sheet so that it could be applied at an industrial scale could be another important area of future work.

The effect of cellulose crystallinity on barrier properties could be further investigated by adding cellulose nanocrystals at increasing doses into MFC films, measuring the oxygen and water vapour barrier properties and studying changes in pore structure of the cellulose films through mercury porosimetry. Studying changes in the pore structure of the films when cellulose nanocrystals were incorporated would help to separate changes from the cellulose nanocrystals filling in void spaces in the MFC films from any changes to barrier properties resulting from increasing the crystallinity of the films. Decreasing the moisture sensitivity of the cellulose could also be investigated in the future through hydrophobization of the cellulose or cross linking of the cellulose to help improve the water vapour barrier properties of the cellulose and to prevent a decrease in barrier properties of the cellulose at high humidity.

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Review

The effect of pre-treatment and process conditions on the gas barrier properties of fibrillated cellulose films and coatings: A review

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ABSTRACT

Microfibrillated cellulose (MFC) is a bio-material produced by disintegrating cellulose fibres into fibrillar components. MFC could offer a sustainable solution to packaging needs since it can form an excellent barrier to oxygen. However, a comprehensive understanding of how MFC characteristics impact barrier properties of MFC films or coatings is required. This article critically reviews how the extent of separation of fibres into fibrils—and any resulting changes to the crystallinity and degree of polymerisation of cellulose—influences gas barrier properties of MFC films or coatings. Findings from publications investigating the barrier performance of MFC prepared through different processes intending to increase the effectiveness of fibrillation are evaluated and compared. The effects of processing conditions or chemical pre-treatments on barrier properties of MFC films or coatings are then discussed. A comparison of reported results showed that morphology and size polydispersity of the cellulose strongly influence the barrier properties of MFC. However, changing the MFC production process to decrease fibril diameter and polydispersity can result in changes to cellulose crystallinity; reduction in fibril length; introduction of bulky functional groups; or increased fibril surface charge: all of which could have a negative impact on the barrier properties of the final films or coatings.

1. Introduction

1.1. The needs for sustainable packaging

Packaging is important to protect contents from damage during transportation and storage. It also provides a barrier layer between the contents and the outside environment. The barrier layer can extend shelf life of food because the transport of gases such as oxygen and water vapour are reduced and leakage of water and oil is prevented. Single use plastics are common in packaging as they can have excellent barrier properties. However, many petroleum based plastics are not biodegradable (Marsh and Bugusu (2007), Rhim et al. (2013)). It is estimated that 275 million tonnes of plastic waste was produced in 2010, of which 12.5 million tonnes may have reached the world's oceans (Jambeck et al., 2015). Plastic waste will remain in the ocean for many years without degrading. This can lead to death of marine life and the production of microplastics which are ingested by sea creatures (Barnes et al., 2009).

More sustainable alternatives to single use plastics include polylactic

acid (PLA), paper, or cardboard which are all biodegradable (Farah et al. (2016), Marsh & Bugusu, 2007, Wang et al., 2018). However, PLA is classed as a low oxygen barrier when compared to other conventional plastics used in packaging (Wang et al. (2018)). Paper and cardboard also have poor barrier properties due to their porous structure and are usually coated when used for food packaging (Marsh and Bugusu (2007), Wang et al. (2018)). For these sustainable packaging materials to be used in food packaging, the barrier properties must be improved. Coating of paper or cardboard based material with polymers such as polyethylene, polypropylene or polyvinyl chloride is commonly used to provide a water vapour barrier. However, this makes the paper difficult to recycle and non biodegradable (Tyagi et al., 2021). Applying a sustainable coating layer which provides good barrier properties to biodegradable polymers or paper and cardboard could help to improve the barrier properties and make a more sustainable packaging alternative.

A material, known as microfibrillated cellulose (MFC), can be used to construct films or coatings with excellent oxygen barrier properties and water vapour barrier properties greater than that of cardboard or paper

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only (Lavoine et al. (2012), Wang et al. (2018)). Section 1.3 describes the parameters used to compare the water and oxygen barrier properties of packaging materials and how the barrier properties of MFC films compare with commercial packaging materials.

1.2. Cellulose and microfibrillated cellulose

Microfibrillated cellulose (MFC) was first produced by Turbak et al. (1983) and Herrick et al. (1983) by repeated mechanical treatment of a cellulose fibre slurry, resulting in a gel network of fibrils. MFC is described as the material made by applying mechanical force to cellulose fibres to split the larger fibre structure into microfibrils or microfibril aggregates. The fibrils also have a high aspect ratio, they are flexible and they contain both crystalline and amorphous regions. As a result of the small size, the surface area of MFC is comparatively much larger than the same mass of cellulose fibres. A chemical pre-treatment can be used to reduce the intensity of mechanical processing needed. The size distribution of the material depends on the production method and pre-treatments used (Eichhorn et al. (2010), Lavoine et al. (2012), Paakko et al. (2007), Siqueira et al. (2010), Turbak et al. (1983)).

An optical micrograph of cellulose fibres is shown alongside a

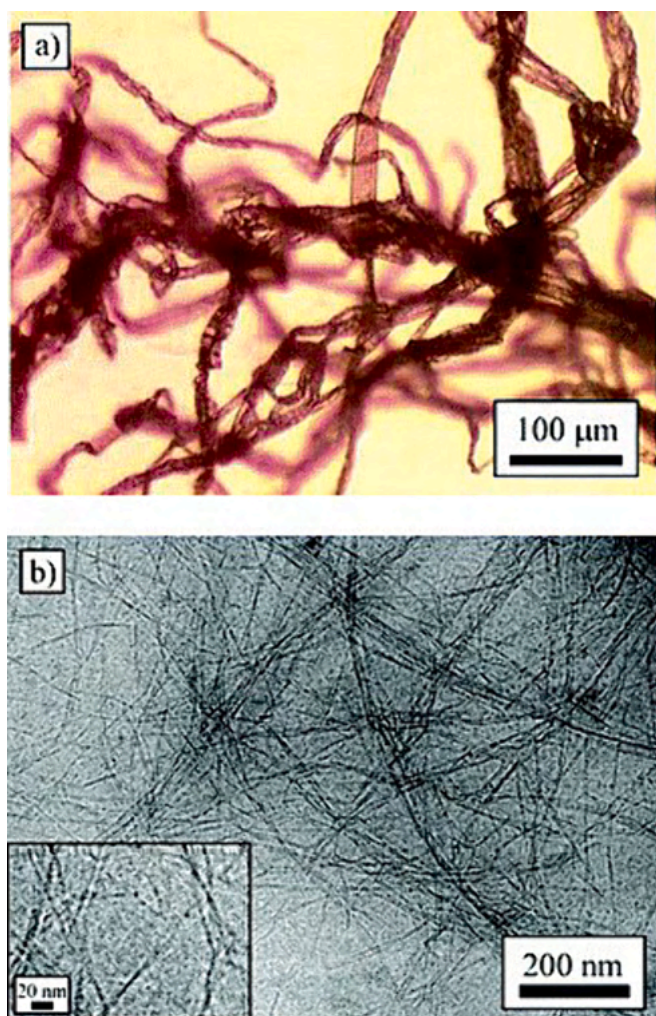


Fig. 1. Optical microscope image of cellulose fibres (a) and TEM image of MFC (b). Reprinted with permission from M. Pääkkö, M. Ankerfors, H. Kosonen, A. Nykänen, S. Ahola, M. Österberg, J. Ruokolainen, J. Laine, P. T. Larsson, O. Ikkala, and T. Lindström (2007), *Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels*, *Biomacromolecules*, 8(6):1934–1941. Copyright 2007 American Chemical Society.

Transmission Electron Microscope (TEM) image of MFC in Fig. 1 (Paakko et al., 2007). The change in morphology from a fibrous structure to a higher aspect ratio, higher surface area fibrillar structure is apparent between the cellulose fibres and MFC.

Applying acid hydrolysis and mechanical treatment to cellulose fibres hydrolyses the amorphous regions of cellulose, producing cellulose nanocrystals (CNC) (Habibi et al. (2010), Lavoine et al. (2012)). The difference in morphology between fibrillated cellulose materials and CNC is shown in Fig. 2. (Bardet et al., 2015).

MFC is also commonly referred to as fibrillated cellulose, nano-fibrillated cellulose (NFC), cellulose nanofibres or cellulose nanofibrils (CNF) (Kangas et al. (2014), Siqueira et al. (2010)). For simplicity, these fibrillated cellulose materials will be referred to as MFC in this review. This review will focus on fibrillated cellulose materials which have been produced from cellulose fibres without an acid hydrolysis phase, therefore not considering the barrier properties of CNCs.

1.3. Barrier properties of food packaging

Oxygen transmission rate (OTR) and water vapour transmission rate (WVTR) describe the rate of oxygen or water vapour transmitted over time per sample area. Related parameters are oxygen permeability (OP) or water vapour permeability (WVP) which are calculated from the transmission rate using the sample thickness and the difference in vapour partial pressure on either side of the film. Eqs. (1)–(3) show how these parameters are calculated (Wang et al., 2018). Film thickness and vapour pressure are not always available in publications and therefore either transmission rate or permeability are used in this review, as reported by the authors.

$$\text{WVTR or OTR} = \frac{\text{mass of water transmitted or volume of oxygen transmitted}}{\text{Area} \times \text{time}} \quad (1)$$

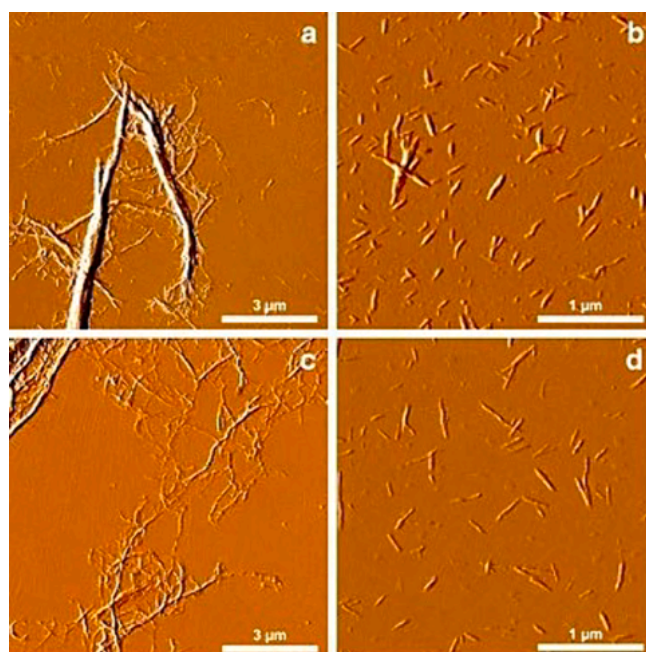


Fig. 2. AFM image of CNF before (a) and after (c) TEMPO mediated oxidation and CNC before (b) and after (d) TEMPO mediated oxidation (adapted) from: Substitution of nanoclay in high gas barrier films of cellulose nanofibrils with cellulose nanocrystals and thermal treatment, R. Bardet, C. Reverdy, N. Belgacem, I. Leirset, K. Syverud, M. Bardet and J. Bras, *Cellulose*, 22, 1227–1241, Springer Nature, 2015, reproduced with permission from SNCC. (Licensed material not part of governing OA license).

$$WVP = \frac{WVTR^* \text{ thickness}}{\text{Saturated vapour pressure}^* \Delta RH} \quad (2)$$

$$OP = \frac{OTR^* \text{ thickness}}{\text{change in oxygen partial pressure}} \quad (3)$$

Fig. 3 shows the OTR and WVTR required for different food packaging applications (Wang et al., 2018). Both oxygen and water vapour barrier properties are commonly needed. Table 1 shows a comparison of the oxygen and water vapour barrier properties of an MFC film with single use plastics commonly used in food packaging. MFC shows low OP, comparable to poly vinylidene chloride or ethylene vinyl alcohol in dry conditions. However, the WVP of MFC films are high compared to other polymers. This limits the effectiveness of MFC in packaging requiring a water vapour barrier.

There have been attempts to improve the water vapour barrier properties of MFC through the addition of another biobased coating layer to provide the water vapour barrier, for example: beeswax or cooked starch (Spence, Venditti, Rojas, Pawlak, & Hubbe, 2011); shellac (Hult et al., 2010); PLA (Koppolu et al., 2019); or alkyl resin (Aulin & Strom, 2013). Alternative strategies to improve the water vapour barrier properties of MFC are increasing the hydrophobicity of the cellulose (Yook et al. (2020), Rodionova et al. (2010)) or adding platey minerals such as montmorillonite or bentonite (Garusinghe et al. (2018), Zheng et al. (2019)).

1.4. Aim and scope of the review

For an in depth review on the production of MFC and the barrier properties of MFC films and coatings, the reader is referred to Lavoine et al. (2012); or for a more recent review of nanocellulose materials in food packaging to Ahankari et al. (2021). The use of MFC in packaging, including chemical modifications aiming to increase hydrophobicity of MFC, was recently reviewed by Hashemzahi et al. (2022). Additional information on the comparison of MFC with other available barrier polymers along with a review of studies looking into oxygen and moisture barrier properties of MFC is given by Wang et al. (2018).

The effect of cellulose morphology on barrier properties of MFC films and coatings is not well understood at present. This review article will focus on studies which have changed MFC production conditions or pre-treatment in an attempt to increase the separation of fibrils from the main fibre. Incidental changes in the cellulose resulting from the attempt to increase separation into fibrils such as changes in crystallinity, degree of polymerisation, surface charge or the introduction of bulky functional

Table 1

Oxygen and water vapour permeabilities of polymers used in food packaging compared to MFC.

Material	OP (cm ³ μm m ⁻² day ⁻¹ kPa ⁻¹)	WVP (g μm m ⁻² day ⁻¹ kPa ⁻¹)
MFC Film	Naderi, Lindstrom, Sundstrom, et al. (2016) 0.04 ± 0.008 @ 23 °C, 50 % RH	Hasan et al. (2021) 15,700 ± 950 @ 23 °C, 100 % to 50 % RH.
Polyethylene terephthalate	Lange and Wyser (2003) 10–50 @ 23 °C, 50 % RH	Cava et al. (2006) 0.013 @ 21 °C, 100 % to 40 % RH.
Polypropylene	Lange and Wyser (2003) 500–1000 @ 23 °C, 50 % RH	Ozcalik and Tihminlioglu (2013) 493 ± 32 @ 37.8 °C, 90 % RH
Poly vinylidene chloride	Lange and Wyser (2003) 0.1–3 @ 23 °C, 50 % RH	Herald et al. (1996) 95 @ 23 °C, 100 % to 55 % RH
Ethylene vinyl alcohol co-polymer	Kang et al. (2018) 0.0223 ± 0.0002 @ 23 °C, 0 % RH	Kang et al. (2018) 699 ± 76 @ 23 °C, 95 % RH
Poly lactic acid	Aulin et al. (2013) 169 @ 23 °C, 50 % RH	Aulin et al. (2013) 386 @ 23 °C, 50 % RH

groups will also be considered. It is vital to understand the relationship between MFC production method, structure and barrier properties so that the most effective materials can be used in food packaging.

In order to present findings from these studies on how MFC properties influence barrier properties, an overview of MFC production methods and chemical and enzyme pre-treatments is provided. This is followed by a discussion on how MFC films provide a gas barrier and a brief overview of MFC characterisation methods. Following this, studies concerning how delamination of cellulose fibres into fibrils affects barrier properties are grouped depending on MFC production, evaluated, and compared.

2. Methods to produce microfibrillated cellulose

Methods to produce MFC have been reviewed comprehensively by Abdul Khalil et al. (2014), Lavoine et al. (2012), Nechyporchuk et al. (2016), Siró and Plackett (2010), and more recently Noremylia et al. (2022) as well as many others. A summary of mechanical processing and chemical pre-treatment methods used by papers presently reviewed to make MFC are shown in Fig. 4.

2.1. Enzyme pre-treatments

To reduce the energy needed to produce MFC from cellulose and to prevent blocking of homogenizers, an enzyme pre-treatment can be used

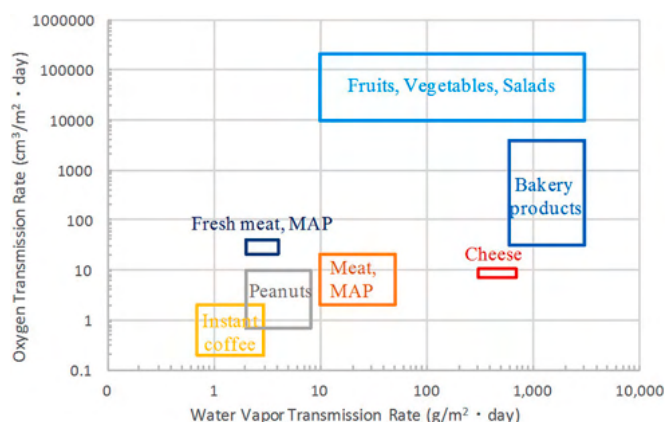


Fig. 3. Barrier properties required from different types of food packaging. Reprinted with permission from: J. Wang, D. J. Gardner, N. M. Stark, D. W. Bousfield, M. Tajvidi, and Z. Cai (2018) *Moisture and oxygen barrier properties of cellulose nanomaterial-based films*, ACS Sustainable Chemistry and Engineering 6 (1):49–70, Copyright 2018 American Chemical Society.

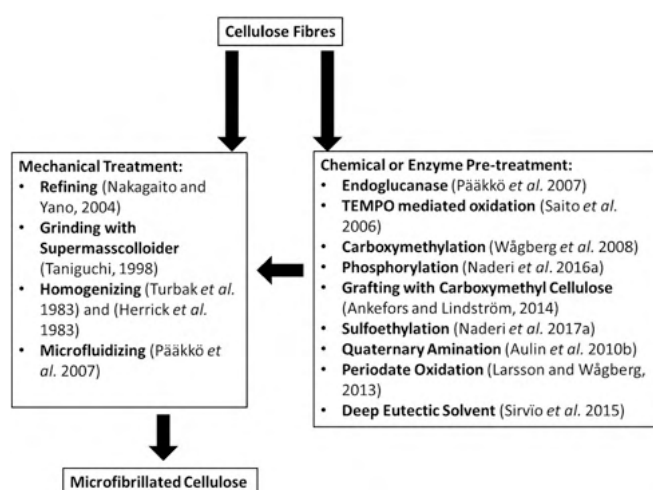


Fig. 4. A flow chart showing commonly used mechanical processing and chemical pre-treatment methods to produce MFC.

(Henriksson et al. (2007), Lavoine et al. (2012), Paakko et al. (2007)). Using enzymes rather than other chemical methods discussed later such as carboxymethylation and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) mediated oxidation may be considered to be more environmentally friendly since no hazardous reagents or solvents are required (Hassan et al. (2010), Hassan et al. (2014)).

The hydrolysis of cellulose to glucose in nature uses a class of enzymes known as cellulases. Endoglucanase enzymes are thought to break random glycosidic bonds within the cellulose fibrils in amorphous regions of the fibre, reducing overall chain length. Amorphous regions of cellulose are more common on the surface of the fibre and occur between crystalline regions of microfibrils. Therefore, the endoglucanase treatment swells the fibre walls, which leads to less energy being required to separate the fibrils during later processing stages. Cellobiohydrolases then act from the ends of cellulose molecular chains and hydrolyse cellulose into smaller, soluble derivatives. Glucosidase then breaks down these soluble cellulose derivatives into glucose (Engstrom et al. (2006), Henriksson et al. (2007), Liu et al. (2009)).

2.1.1. Deep eutectic solvents

A deep eutectic solvent refers to a mixture of materials where the melting point of the mixture is lower than any individual component as a result of strong hydrogen bonding (Sirvio et al. (2015)). MFC was produced by heating cellulose pulp in a mixture of choline chloride and urea which forms a deep eutectic solvent prior to passing through a microfluidizer by Sirvio et al. (2015). The deep eutectic solvent treatment

allowed the pulp to pass through the microfluidizer without clogging which was not possible for untreated pulp. Li et al. (2017) found that pre-treatment of cellulose fibres with deep eutectic solvents resulted in an increase in fibre width which suggested that the fibres were swelling, possibly due to hydrogen bonds forming between cellulose and the components of the deep eutectic solvent mixtures.

2.2. Chemical pre-treatments

Using a chemical pre-treatment before mechanical processing can help to separate cellulose into individual nano sized fibrils (Saito et al. (2007)). Chemical treatments aiming to increase the degree of cellulose fibrillation in studies discussed as part of this review are summarised in Fig. 5. For a more comprehensive review of chemical pre-treatments used on cellulose prior to fibrillation, readers could refer to the review by Nechyporchuk et al. (2016).

3. Characterisation of microfibrillated cellulose

This review paper focuses on how different cellulose pre-treatments and MFC production methods affect the barrier properties of MFC films and coatings. Therefore, it is important to characterise the MFC so as to understand the effects of the size distribution and morphology of cellulose on barrier properties. The same methods of MFC characterisation are not used in every study discussed in the present review, making direct comparisons about MFC characteristics and barrier properties

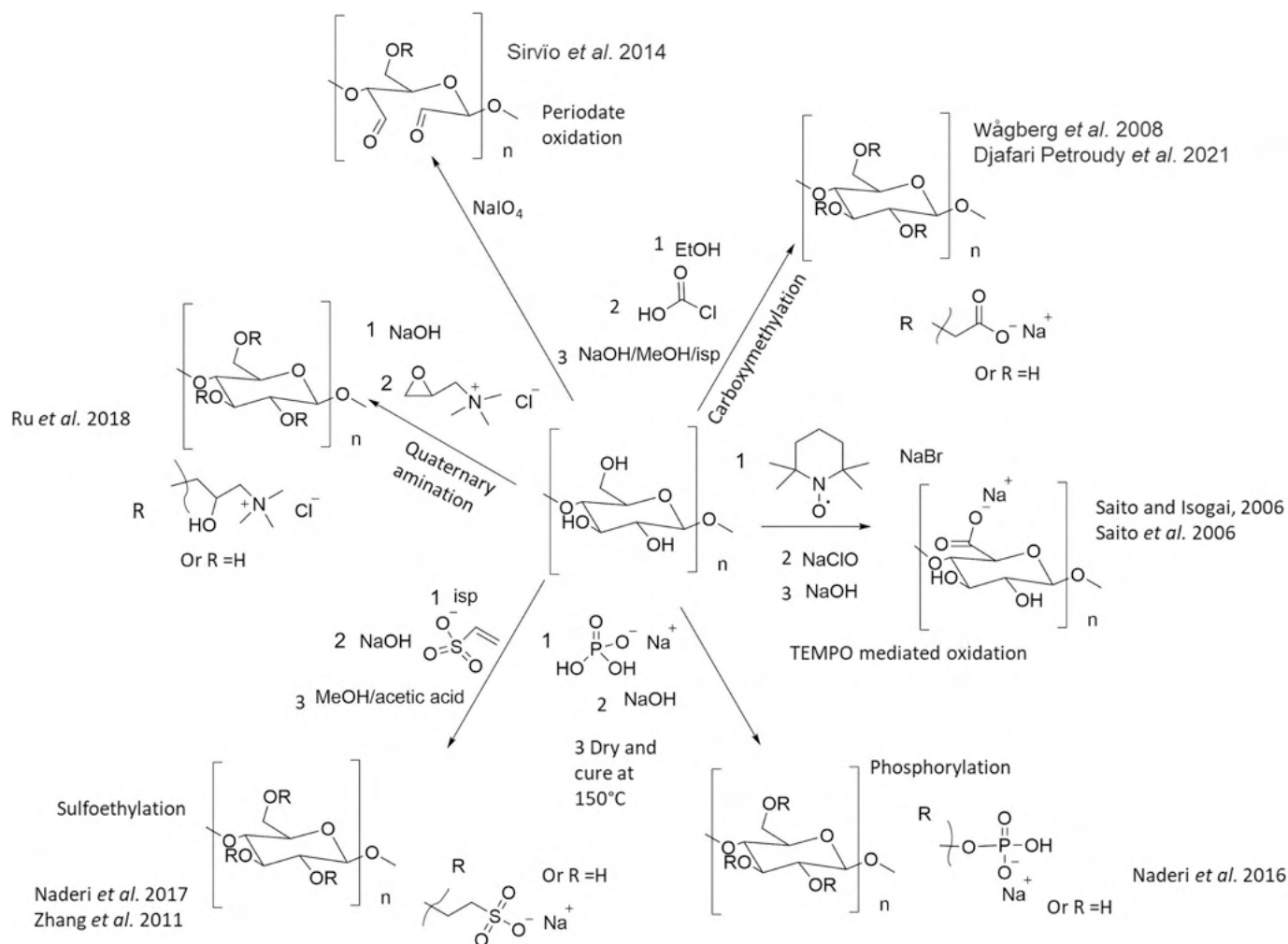


Fig. 5. Chemical cellulose modifications used as pre-treatments in MFC production relevant to papers discussed in Section 5 of the review. Compiled using Chemdraw software from sources listed in the figure.

across different publications difficult. For detailed discussion of characterisation of MFC, the reader is referred to [Kangas et al. \(2014\)](#) or [Osong et al. \(2016\)](#). For a specific discussion on characterising the crystallinity of cellulose, the reader is referred to [Park et al. \(2010\)](#).

Table 2 shows a summary of the advantages and disadvantages of different characterisation methods used by studies discussed in this review.

4. Barrier properties of microfibrillated cellulose

Gases are thought to travel through polymer films via dissolution in the polymer matrix, diffusion across a concentration gradient, and evaporation on the other side of the film. The transport through the polymer therefore depends on the solubility of the gas and how easy it is for the molecules to travel through the polymer matrix. The solubility of a gas through a polymer depends on chemical interactions between the gas and functional groups of the polymer since favourable interactions allow dissolution. However, strong interactions between polymer chains

can slow diffusion since the chains are held closely and mobility is restricted. Increasing crystallinity of the polymer decreases diffusivity because crystalline regions are impermeable and increasing the fraction present increases the path length for diffusing gases. Crystalline regions further restrict transport because they reduce the mobility of surrounding amorphous polymer chains, leading to decreased free volume within the polymer ([Lagaron et al. \(2004\)](#)). Comparing an MFC film or coating to a polymer film, it appears that factors such as changing the physical structure and porosity of the MFC film, altering the crystallinity of the cellulose, and altering the chemical properties of the cellulose would all have an influence on barrier properties of the film.

With regards to the physical structure of an MFC film, [Syverud and Stenius \(2009\)](#) found that MFC films have a low air permeability and suggested that this meant there were no connecting pore channels running from one side of the MFC film to the other. [Aulin et al., 2010](#) measured the density of films made from MFC produced by carboxymethylation followed by microfluidization as $1.57 \pm 0.03 \text{ g cm}^{-3}$ which is between the densities of crystalline and amorphous cellulose, therefore, implying that porosity within the films is low and that there is little pore space for diffusing gases to travel through. SEM images of MFC film surfaces and cross sections shown by [Aulin et al. \(2010\)](#) and [Minelli et al. \(2010\)](#) show that there is surface porosity between fibrils but a dense layered middle structure. An example is shown in [Fig. 6](#) ([Aulin et al. \(2010\)](#)). The work of [Aulin et al. \(2010\)](#), [Minelli et al. \(2010\)](#) and [Syverud and Stenius \(2009\)](#) suggests that the physical structure and porosity of the MFC film is one of the key reasons for the excellent barrier properties. This suggests that changing the physical structure of the cellulose by increasing separation of fibrils from fibres may lead to improvements in barrier properties of MFC films.

The porosity of MFC films has been studied using Positron Annihilation Lifetime Spectroscopy (PALS). For example, [Fukuzumi et al. \(2011\)](#) used PALS to measure the averaged pore size of MFC films made from TEMPO oxidised cellulose—which was 0.47 nm at 0 % relative humidity (RH)—and these pores did not connect throughout the film. [Roilo et al. \(2017\)](#) also used PALS to study the pore size of TEMPO oxidised MFC films and found that the size of pores, in this paper described as diameters of long spaces between fibrils, was approximately 0.31 nm (RH not provided). [Roilo et al. \(2017\)](#) used a different method of analysis of the PALS data to account for the geometry of long channels between nanofibrils. [Torstensen et al. \(2018\)](#) also used PALS to characterise TEMPO oxidised cellulose films but in contrast to the

Table 2

Overview of MFC characterisation methods used in studies discussed in this review.

Method	Advantages	Disadvantages
Fibre image analyser	A quantitative description of MFC, allows comparison between samples.	Some fibrils are too small to be detected by fibre image analysers which work through optical imaging (Padberg et al., 2016).
Microscopy: Optical, SEM, TEM or AFM	Morphology of the material can be understood (Kangas et al., 2014).	Extensive time required to image representative samples (Osong et al., 2016).
X-ray diffraction	Crystallinity index of cellulose is measured, which can be used to compare samples (Park et al., 2010).	The commonly used peak height determination of crystallinity index may not give a true quantitative value (Park et al., 2010).
Mass percentage remaining in supernatant after centrifuging	A quantitative measurement of mass percentage of fine material which can be used to compare samples (Taipale et al., 2010).	No structural information is provided about material remaining in the supernatant (Kangas et al., 2014).
Viscosity of MFC suspensions	Increasing separation of fibres into fibrils can be estimated by increasing suspension viscosity (Schenker et al., 2019).	Fibril length can be an important factor in measured viscosity so it is not always clear if a lower viscosity is due to lower fibrillation or reduced fibril length (Kangas et al., 2014).
Light transmittance of MFC suspensions	A quantitative comparison between samples as finer cellulose samples have higher transmittance (Saito et al., 2006).	If the particle diameter approaches the light wavelength, scattering can increase which results in a lower transmittance (Kangas et al., 2014).
Specific surface area through Congo red dye absorption	A quantitative comparison of surface area between cellulose samples (Ougiya et al., 1998).	Absorption of Congo red dye can be affected by crystallinity and lignin content of cellulose which may affect results (Ougiya et al. (1998) , Spence, Venditti, Rojas, Habibi, and Pawlak (2011)).
Degree of polymerisation	Degree of polymerisation measurement compares the length of the cellulose chains or the degradation of the cellulose molecular structure (Kangas et al. (2014) , Iwamoto et al. (2007)).	Degree of polymerisation can give an estimate of fibril length but the true value can be greater than cellulose chain length suggests (Shinoda et al., 2012).

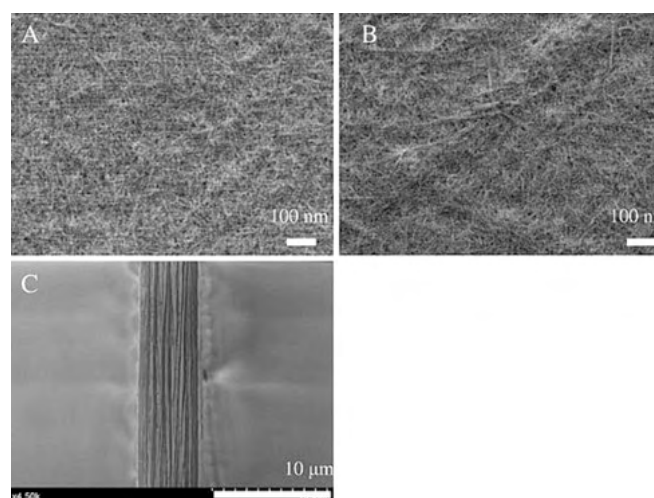


Fig. 6. SEM images of surface (A,B) and cross section (C), of MFC films. Reprinted from: *Oxygen and oil barrier properties of microfibrillated cellulose films and coatings*, C. Aulin, M. Gallstedt, T. Lindstrom, Cellulose 17(3):559–574, 2010, reproduced with permission from SNCC. (Licensed material not part of governing OA license).

publications above described the pores as spaces between amorphous cellulose chains rather than between cellulose fibrils. This value was 0.215 nm at 0 % RH. In contrast, Orsolini et al. (2015) measured the average pore diameter of MFC films through mercury intrusion porosimetry as 28.6 ± 2.3 nm. However, Orsolini et al. (2015) used MFC produced through mechanical only processing to form the films without the TEMPO mediated oxidation step, leading to a material with fibril diameters below 100 nm. Roilo et al. (2017) measured average fibril diameter as 4 nm, showing a significant fibril diameter size difference between the two types of materials which may account for the significant difference in measured pore size.

Roilo et al. (2017) further studied the influence of pore size on permeability by measuring the transport of hydrogen gas and helium gas as well as nitrogen and carbon dioxide. No transmission of carbon dioxide or nitrogen gas could be measured but permeability of $\text{He}_{(g)}$ and $\text{H}_{2(g)}$ were 0.4 ± 0.1 and $0.1 \pm 0.03 \text{ mL } \mu\text{m}^{-2} \text{ day}^{-1} \text{ kPa}^{-1}$ respectively. The kinetic diameters of $\text{He}_{(g)}$ and $\text{H}_{2(g)}$ are 0.26 and 0.289 nm whereas CO_2 and N_2 have kinetic diameters of 0.364 nm and 0.33 nm (Roilo et al., 2017). Roilo et al. (2017) concluded that helium and deuterium gas were able to pass through the MFC layer because their kinetic diameters were smaller than the size of the pores but larger gas molecules could not pass through at a rate high enough to be measured. This experiment could explain why MFC films made from finely dispersed cellulose fibrils such as those made through TEMPO mediated oxidation show excellent oxygen barrier properties. The oxygen molecules may be too large to travel through elongated channels between fibrils as proposed by Roilo et al. (2017). However, MFC made from coarser or more polydisperse material is likely to form films with a higher degree of physical porosity and therefore allow the transport of oxygen. In this case, the mechanism for the oxygen barrier may be the lack of connecting porosity as suggested by Aulin et al., 2010, Minelli et al. (2010), Syverud and Stenius (2009).

Aulin et al. (2010) and Syverud and Stenius (2009) suggested that the crystalline regions of cellulose may help to improve the barrier properties of MFC films. However, Belbekhouche et al. (2011) found that films of MFC had lower oxygen permeability than films made from CNC despite the CNC having a higher crystallinity. The authors suggested this could be partly due to chemical differences between the materials, but also because the MFC forms a more entangled, dense network with little connecting porosity which is more effective in inhibiting gas diffusion.

4.1. The effect of water on MFC barrier properties

MFC films can be good barriers to oxygen at low RH but, at high RH, the oxygen permeability increases. MFC is a hydrophilic material due to many accessible hydroxyl groups on the fibril surfaces which leads to water sorption at high humidity (Aulin et al. (2010), Minelli et al. (2010)). This water sorption reduces the hydrogen bonding between fibrils and allows swelling of the films which may then provide more open porosity allowing for oxygen diffusion (Aulin et al. (2010)). The increase in oxygen permeability at high RH is observed also for ethylene vinyl alcohol (EVOH) due to an interruption in hydrogen bonding by water molecules (Lagaron et al. (2004)). Torstensen et al. (2018) used PALS to measure the size of free volume holes within TEMPO oxidised cellulose films, which the authors described as spaces between amorphous cellulose chains. Upon increasing relative humidity, there was an initial decrease in the size of free volume holes, followed by an increase. This led to the explanation from the authors that initially at low RH, water binds between cellulose molecules and as the RH further increases, the pores swell which pushes chains apart and eventually leads to increased porosity within the film. Further evidence for swelling leading to increasing oxygen transmission at increased relative humidity was seen by Miettinen et al. (2014) who found that the thickness of an MFC film, measured through X-ray microtomography, increased as the relative humidity increased. For further discussion on the effect of

moisture on oxygen barrier properties of MFC films, the reader is directed to Section 5.4.

The deterioration in oxygen barrier at high RH is a significant issue which needs to be considered when replacing other barrier materials with MFC. Numerous studies have used hydrophobization of MFC in order to reduce the water vapour transmission rate of the material or to reduce the oxygen transmission rate at high relative humidity. The effect of hydrophobization of cellulose on the barrier properties of MFC films is beyond the scope of the present review, the reader is directed to the work of Yook et al. (2020), Rodionova et al. (2010), Peresin et al. (2017), Chinga-Carrasco et al. (2012) and Li et al. (2019) for examples of this strategy.

5. The effect of pre-treatment and process conditions on the barrier properties of MFC

5.1. Increasing mechanical processing

5.1.1. Increasing the intensity of one fibrillation method with no chemical pre-treatment

Publications studying the effect of increasing mechanical treatment without any chemical pre-treatment to help facilitate fibrillation are summarised in Table 3.

Padberg et al. (2016) compared the OTR of MFC cast films where the MFC was passed through a Supermasscolloider grinder for an increasing number of times. The study found that the films produced from MFC made from the ten passes through the grinder presented excellent oxygen barriers beyond the sensitivity of the test whereas the films produced from MFC made from nine passes were poor oxygen barriers. This effect was linked to the increased %Fines content and decreased large fibre fragments in the MFC observed in the fibre analyser data. Furthermore, mercury porosimetry analysis showed a decrease in pore volume in MFC films between 9 and 10 grinder passes. In a similar study, Nair and Yan (2015) studied the effect of increasing number of passes on the water vapour permeability of MFC films and found that initially, there was a significant decrease in water vapour permeability as the number of passes through the grinder increased but after 3 passes a plateau was reached. Also looking into increasing the degree of fibrillation by passing cellulose fibres through a Supermasscolloider grinder with increasing number of passes, Bessonoff and Paltakari (2015) found that for low film thicknesses, increasing number of passes from 4 to 9 decreased OP. However, the OP difference between the samples significantly decreased as the film thickness increased. The results of Bessonoff and Paltakari (2015) imply that film thickness affects the influence of fibrillation on barrier properties of MFC films.

By passing cellulose fibres through a disc refiner an increasing

Table 3

Summary of previous studies on the effect of increasing intensity of mechanical treatment on barrier properties of MFC films or coatings without a chemical pre-treatment stage.

Reference	MFC production	Findings
Padberg et al. (2016)	Grinding using Supermasscolloider	Increasing number of passes decreased OTR.
Nair and Yan (2015)	Grinding using Supermasscolloider	Increasing number of passes decreased WVTR but effect plateaued.
Bessonoff and Paltakari (2015)	Grinding using Supermasscolloider	At low film grammage, increasing number of passes decreased OTR.
Juntunen (2021)	Increasing number of passes through refiner	Increasing number of passes decreased OTR and hexane vapour transmission.
Wei et al. (2023)	Increasing number of passes through microfluidizer after a Supermasscolloider grinding stage.	WVP decreased at 50 % RH for MFC films, no effect measured for OP.

number of times to make increasingly fine MFC, Juntunen (2021) found that increasing the number of passes decreased the hexane vapour transmission rate of MFC coated onto filter paper. Similarly, there was an abrupt and significant reduction in oxygen transmission rate. This decrease in hexane vapour transmission rate corresponded with an increase in MFC suspension viscosity, suggesting that the higher degree of separation of the cellulose into fibrils was the reason for the decreasing hexane vapour transmission rate. This trend is similar to the findings of Padberg et al. (2016) and implies that the development of barrier properties occurs once the cellulose is sufficiently delaminated that it forms networks with no connecting porosity.

In a similar study to Juntunen (2021), Nair and Yan (2015) and Padberg et al. (2016), Wei et al. (2023) recently investigated how increasing the number of passes of Supermasscolloider ground MFC through a microfluidizer affected the barrier properties of MFC films. The study found that at 50 % RH, increasing the number of passes through the microfluidizer decreased WVP of the films, supported by an increase in density of films as number of passes increased. However, when accounting for variation there was no significant decrease in WVP at 90 % RH or OP at 50 % or 90 % RH.

Both Padberg et al. (2016) and Wei et al. (2023) investigated the effects of changes in cellulose crystallinity through mechanical processing since crystallinity is thought to be an important factor in the barrier properties of polymers. Wei et al. (2023) measured crystallinity of the MFC films through Raman spectroscopy and found that crystallinity index decreased as the number of passes through the microfluidizer increased. The authors suggested that this decrease in crystallinity did not have a negative effect on the water vapour barrier properties of the films and that the increasing density of the film resulting from finer fibrils had a larger impact on the barrier properties than decreasing the crystallinity. Similarly, Padberg et al. (2016) measured crystallinity of MFC films through X-ray diffraction and found that the crystallinity index decreased when increasing number of passes through the Supermasscolloider grinder were used. However, a detrimental effect on the OTR was not seen and therefore it was assumed that the changes in physical structure of the film from increasing cellulose fibrillation had a greater impact on the oxygen barrier properties than decreasing cellulose crystallinity.

Addressing the effect of larger cellulose fibre fragments on oxygen barrier properties, Herrera et al. (2018) compared the oxygen transmission rates of films produced from MFC produced via TEMPO mediated oxidation followed by microfluidization with and without removing larger cellulose particles via centrifugation. The authors found that films made from the unfractionated samples had a higher OTR at 30 % and 50 % RH than the films made from the fractionated samples. This suggests that large fragments may have a disruptive effect on MFC film barrier properties. This could explain why the effect of increasing fibrillation on MFC barrier properties appears to plateau- once large fibres are removed, a dense network can form with low connecting porosity.

A review article by Naderi and Lindstrom (2017) suggested that increasing separation of cellulose fibres into fibrils has an initial effect in improving barrier properties of MFC films, but once a very fine material is reached, there is no further benefit in increasing the mechanical treatment intensity. This idea is supported by the results of Nair and Yan (2015), Padberg et al. (2016), and Wei et al. (2023). The work of Besonoff and Paltakari (2015) suggests that the film thickness may play a role in the threshold degree of fibrillation required to form optimum barrier properties. Furthermore, Roilo et al. (2017) suggested that the method of transport through MFC depends on the pore size within the material and gases can diffuse through the pore space if the pores are large enough. Therefore, if the degree of fibrillation is high enough to prevent gas travelling through pore space, there is no further benefit to increasing fibrillation. Chinga-Carrasco and Syverud (2012) found that increased density of MFC films led to decreased OTR which supports the theory that decreasing pore space is beneficial as denser films have less

pore space.

Results from Nair and Yan (2015) and Padberg et al. (2016) appear to support the hypothesis that initially increasing the fibrillation of cellulose improves gas barrier properties, but this effect does not continue as the fibrillation increases. This could provide valuable insight into the mechanism of the gas barrier of MFC films. As described in Section 4, Aulin et al. (2010), Minelli et al. (2010) and Syverud and Stenius (2009) suggest MFC forms barrier layers because there is no connecting porosity through the MFC layer. Therefore, it could be the case that for coarse MFC with large fibre fragments and few very fine fibrils, there remains some connecting porosity within the layer which allows the diffusion of gases. As the degree of fibrillation increases, the tortuosity of the diffusion pathway increases, increasing the path length and reducing the number of possible routes. Eventually there is no remaining connecting porosity in the MFC layer and as such a plateau in gas barrier properties is reached. This implies that any remaining diffusion through the MFC film may be taking place through a different mechanism.

Furthermore, the examples of Nair and Yan (2015) and Padberg et al. (2016) highlight an important difference between the oxygen and water vapour barrier properties of MFC films. While Padberg et al. (2016) found that increasing the fibrillation led to no detectable transmission of oxygen, Nair and Yan (2015) found that there was a plateau in water vapour permeability as the extent of disintegration of the cellulose fibres increased. This plateau value of water vapour permeability seen by Nair and Yan (2015) could mean there was no remaining connecting porosity within the film for the water vapour to diffuse through and the constant water vapour permeability could have been the amount of water that could sorb through the amorphous regions of cellulose fibres as explained by Belbekhouche et al. (2011) and Okubayashi et al. (2004).

5.1.2. The effect of different mechanical treatments

A summary of investigations into how different mechanical treatments, without a chemical pre-treatment, affect the barrier properties of MFC films and coatings is shown in Table 4.

The studies of Hasan et al. (2021) and Kumar et al. (2014) both compared the oxygen and water vapour barrier properties of films made from MFC produced by refining only and MFC produced with an additional Supermasscolloider grinding step. Kumar et al. (2014) found that the additional grinding stage did not decrease oxygen or water vapour transmission rates of MFC films when accounting for standard deviation within the results. However, Hasan et al. (2021) reported a statistically

Table 4

Findings from literature studies on the effect of increasing mechanical treatment on barrier properties after a chemical pre-treatment.

Reference	MFC production	Findings
Spence, Venditti, Rojas, Habibi, and Pawlak (2011)	MFC produced through different mechanical treatments.	Refining decreased WVTR of MFC compared to pulp only. Additional mechanical treatment stages have different effects on WVTR.
Hasan et al. (2021)	Refining or refining followed by grinding using Supermasscolloider.	Decrease in OP and WVP after additional grinding stage compared to refining only.
Kumar et al. (2014)	Refining or refining followed by grinding with Supermasscolloider.	Small decrease in WVTR and OTR with additional grinding stage but not larger than variation in results.
Spence et al. (2010)	Refining or refining followed by homogenizing.	Refining effective in reducing WVTR compared to pulp. Extra homogenizing stage only decreased WVTR for some pulp types.
Espinosa et al. (2020)	Refining followed by twin screw extrusion, homogenization or grinding.	Little difference in WVTR or OTR, when accounting for variation, between MFC production methods.

significant decrease in OP and WVP when using the MFC from the additional grinding stage compared to refining only. Kumar et al. (2014) found that the MFC produced by refining with a grinding stage had more fine fibrils visible in SEM images than MFC produced by refining only. Similarly, Hasan et al. (2021) measured smaller fibril diameters for the ground MFC and a narrower fibre distribution. The difference in results could be explained by the fact that the two studies used different pulp types which may have different relationships between fibrillation and barrier properties.

Similarly, Spence, Venditti, Rojas, Habibi, and Pawlak (2011) found that a refining treatment significantly reduced WVTR of films compared to untreated pulp only and that a further decrease in WVTR was observed after an additional grinding treatment with a Supermasscolloider or a homogenizing treatment. The WVTR of a sample produced through grinding with a Supermasscolloider only was also measured and it was higher than that of the sample made with a refining pre-treatment. In agreement with these conclusions, Spence et al. (2010) investigated the effect of a refining pre-treatment followed by homogenization on different pulp samples. The study found that WVTR of films produced from the samples decreased significantly after refining compared to the pulp only and decreased further after the homogenization treatment.

The studies of Spence et al. (2010) and Spence, Venditti, Rojas, Habibi, and Pawlak (2011) both use the absorption of Congo red dye as a measure of the specific surface area of MFC. In brief, this method was performed by adding Congo red dye into MFC suspensions, and centrifuging after incubation. UV-vis spectroscopy was then used to calculate the concentration of dye in the supernatant and therefore the amount of dye that had adsorbed onto the cellulose (Spence et al., 2010). This quantitative measure of degree of fibrillation was used to plot the WVTR/thickness measurements given in both papers against the specific surface area of the MFC in Fig. 7. A general trend of increasing surface area leading to decreasing WVTR before appearing to reach a plateau is shown in the graph. This agrees with the results from Nair and Yan (2015) which show a similar trend of increasing fibrillation leading to decreased WVTR then reaching a plateau.

Spence, Venditti, Rojas, Habibi, and Pawlak (2011) found that specific surface area of fibrils measured through absorption of Congo red dye significantly increased after the refining pre-treatment and further increased after grinding. However, the sample produced through grinding only had a higher surface area than that made with a refining

pre-treatment which suggests higher fibrillation but also presented a higher WVTR. It is possible that this high surface area was due to more very fine fibrils being present, but there may still have been some large fibre fragments which caused disruption in the film and increased WVTR. In addition, Spence, Venditti, Rojas, Habibi, and Pawlak (2011) also found that microfluidization post refining did not lead to a decrease in WVTR for bleached pulp, despite increasing specific surface area of the MFC. For unbleached pulp samples, microfluidization did produce a decrease in WVTR, but the WVTR values were higher than the bleached pulp to begin with. This highlights that multiple factors including chemical differences between pulp types can affect how barrier properties of MFC vary with fibrillation.

Espinosa et al. (2020) compared different mechanical treatments to produce MFC after refining pulp. The authors found that the percentage of nanofraction of pulp measured through centrifugation was lower for both the unbleached and bleached pulp produced through twin screw extrusion than homogenization or grinding. The MFC produced through homogenization had the lowest fibril diameter in both bleached and unbleached pulps. However, when accounting for variation there was little difference between OTR values for the MFC produced through different processes. This result highlights that finding a measurement to explain and predict barrier properties of MFC is elusive due to difficulty in characterising the material (Kangas et al. (2014)).

5.1.3. Increasing intensity of mechanical fibrillation after a chemical pre-treatment

A summary of six studies investigating the effect of increasing mechanical processing on the barrier properties of MFC films or coatings after a chemical pre-treatment on the fibres designed to enhance fibrillation is shown in Table 5.

Aulin et al. (2010) and Siró et al. (2011) used a carboxymethylation pre-treatment and subsequently measured oxygen transmission rate or oxygen permeability of MFC films made through increasing number of passes through a microfluidizer or homogenizer. Neither study found a significant improvement in oxygen barrier properties with increasing numbers of passes through the homogenizer or microfluidizer despite the presence of fewer large fibre aggregates in both cases. For example, Aulin et al. (2010) found no significant decrease in OTR between 1 and 10 passes through the microfluidizer. Similarly, Siró et al. (2011) found no significant decrease in OP when the number of passes of carboxymethylated cellulose through a homogenizer was increased from 3 to 5

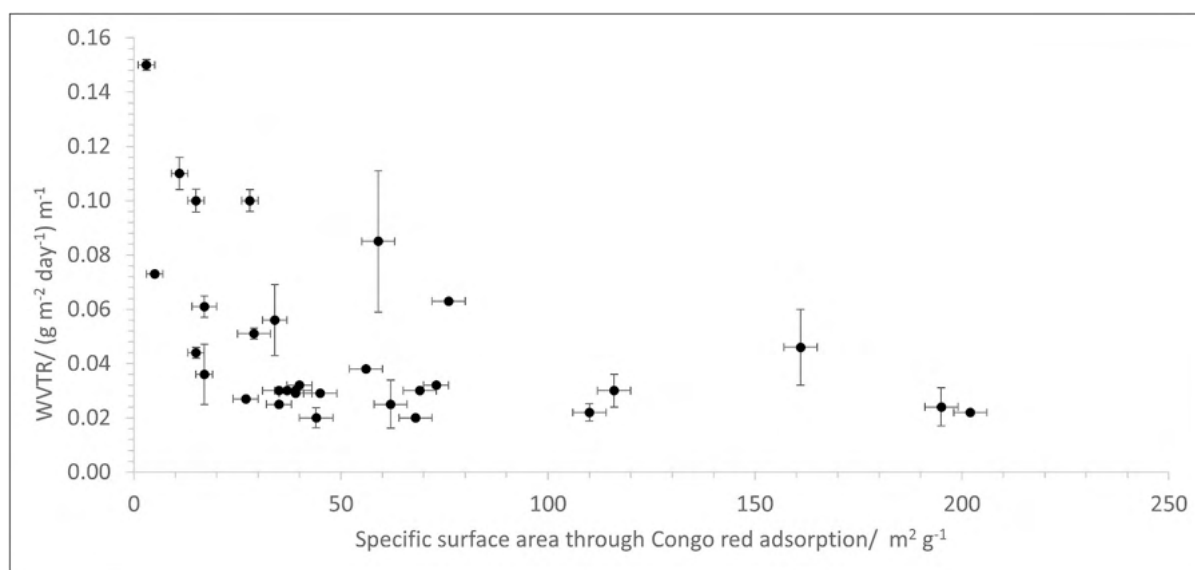


Fig. 7. Graph of WVTR/ thickness as a function of the specific surface area of MFC measured through the absorption of Congo red dye. Graph compiled from data from Spence et al. (2010) and Spence, Venditti, Rojas, Habibi, and Pawlak (2011). Error bars refer to standard deviations given in the papers.

Table 5

Findings from literature studies on the effect of increasing mechanical treatment on barrier properties after a chemical pre-treatment.

Reference	MFC production	Findings
Aulin et al. (2010)	Carboxymethylation followed by homogenizing.	Increasing passes through homogenizer did not decrease OTR.
Siró et al. (2011)	Carboxymethylation followed by homogenizing.	Increasing number of passes did not decrease OP.
Naderi et al. (2015)	Grafting CMC followed by microfluidizing.	Increasing number of passes decreased OP.
Kumar et al. (2014)	TEMPO mediated oxidation followed by homogenizing.	Increasing number of passes did not decrease OTR.
Fukuzumi et al. (2013)	TEMPO mediated oxidation followed by homogenizing and sonicating.	Increasing mechanical treatment intensity increased OTR and did not affect WVTR.
Naderi, Lindstrom, Flodberg, et al. (2016)	Phosphorylation followed by microfluidizing.	Increasing number of passes had different effects depending on degree of substitution and relative humidity of testing environment.

passes. This contradicts the conclusions of Padberg et al. (2016) where it was suggested that decreasing oxygen transmission rate was partially due to fewer aggregates of fibres. This may be due to the carboxymethylation pre-treatments leading to smaller fibril diameters than the initial coarsest samples used in the studies of Hasan et al. (2021), Kumar et al. (2014), Nair and Yan (2015), Padberg et al. (2016). Therefore, increasing degree of fibrillation by increasing the number of mechanical treatment stages did not lead to an improved oxygen barrier, possibly because the surface area of the cellulose and degree of degradation was already high enough to assemble a network with no connecting porosity and therefore continuing to decrease fibril diameter did not affect barrier properties (Aulin et al., 2010). This agrees with the conclusions of Naderi and Lindstrom (2017) that when the degree of fibrillation reaches a high enough level, further treatment of the cellulose does not improve barrier properties.

A similar study can be seen in Naderi et al. (2015) where carboxymethyl cellulose was grafted to cellulose fibres as a pre-treatment before passing through a microfluidizer with increasing number of passes. After 1 pass the oxygen transmission rate was too high to be measured but after 5 passes was very low, suggesting that after 1 pass through the microfluidizer, the MFC was not fibrillated enough to form a dense network. The results may be different from Aulin et al. (2010) and Siró et al. (2011) because possibly the carboxymethyl cellulose grafting pre-treatment was not as effective at dispersing fibrils as the carboxymethylation of cellulose, resulting in an initial sample with a low degree of fibrillation compared to the other studies.

Similarly Naderi, Lindstrom, Flodberg, et al. (2016) phosphorylated cellulose and then microfluidized with increasing number of passes and found that the MFC sample made from cellulose with the lowest degree of phosphate substitution did not form a measurable oxygen barrier after 1 pass through the microfluidizer but did form an effective oxygen barrier after 2 passes, again suggesting that the increased degree of fibrillation from the additional microfluidization pass produced a network of MFC with little connecting porosity. However, increasing to 6 passes through the microfluidizer led to a failed reading for oxygen permeability at 80 % RH and an increase in OP at 50 % RH. The authors suggested this could be due to a reduction in fibril length from over processing, which was supported by AFM images of the MFC samples.

An interesting study which purposefully examined whether increasing mechanical processing can degrade barrier properties of films was performed by Fukuzumi et al. (2013). A TEMPO mediated oxidation pre-treatment was applied to cellulose fibres, followed by the application of three different mechanical treatment methods. The aim was to vary intensity of the mechanical treatment to intentionally cut the fibrils

so that the effect of fibril length on barrier properties could be studied. The study found no difference in water vapour permeability of thin layers of MFC coated on PET, but did find that the longer fibrils had a lower oxygen permeability which the authors suggested was due to higher crystallinity. This study suggests that decreasing the length of the fibrils has some impact on the gas barrier properties. Therefore, it may be that decreasing fibril width is not the only factor that affects barrier properties- potentially a high fibril length and crystallinity is also needed. Table 6 shows the measured average fibril lengths, the degree of polymerisation and crystallinity index. The results show that the oxygen transmission rate began to increase as the length decreased below 1100 nm, the degree of polymerisation below 400 and the crystallinity index below 0.64.

The effect of fibril length was not extensively discussed in other studies, which may be due to difficulties in measuring fibril length (Naderi & Lindstrom, 2017). Kumar et al. (2014) found that a TEMPO oxidised MFC sample formed films with improved barrier properties after a second homogenization stage compared to the first despite no visible decrease in fibril diameter and a decrease in length. However, the authors suggested that the alkaline TEMPO oxidation treatment used in this case was harsh which resulted in rigid, rod like particles. Potentially, the homogenization stage increased their flexibility. An observation from Naderi, Lindstrom, Flodberg, et al. (2016) that increasing number of passes through a microfluidizer after phosphorylation of cellulose increases the OP of MFC films, possibly due to a reduction in fibril length, supports the findings of Fukuzumi et al. (2013).

5.2. The effect of chemical or enzyme pre-treatment

5.2.1. The influence of TEMPO mediated oxidation on the barrier properties of MFC

The results from studies discussed in the next section investigate the effect of TEMPO mediated oxidation on the barrier properties of MFC films or coatings compared to mechanical treatments only. Literature findings are summarised in Table 7.

Jiménez-López et al. (2020) and Kumar et al. (2014) showed that films made from mechanically produced only MFC can form a superior water vapour barrier to TEMPO oxidised samples. In addition, Bessonoff and Paltakari (2015), Guivier et al. (2023) and Kumar et al. (2014) found that there was no significant improvement in oxygen barrier properties for films made from TEMPO mediated oxidation MFC compared to mechanical only MFC when accounting for variation in measurements. This could be for several reasons. Jiménez-López et al. (2020) suggest that the difference could be due to a reduced crystallinity of the cellulose measured in their study following the TEMPO mediated oxidation process. Jiménez-López et al. (2020) also proposed that the additional carboxyl groups created by the TEMPO mediated oxidation process lead to a stronger interaction with water vapour and this is what increases the WVP. This hypothesis was supported by fitting of water vapour sorption isotherms which showed that there was a stronger tendency to bind water for TEMPO mediated oxidation samples. Kumar et al. (2014) suggest that the TEMPO mediated oxidation process may reduce the flexibility of the cellulose, therefore reducing entanglements within the network. This is similar to the argument used by

Table 6

Length, degree of polymerisation (DP) and Crystallinity index (CrI) of MFC samples used in oxygen barrier testing OTR and WVTR values represent values read from graphs in the article of MFC films coated on PET measured at 0 % Relative Humidity. All data sourced from Fukuzumi et al. (2013).

Length/ nm	DP	CrI	OTR (ml m ⁻² day ⁻¹ kPa ⁻¹)	WVTR (g m ⁻² day ⁻¹ kPa ⁻¹)
200	250	0.56	0.005	0.028
680	350	0.59	0.0014	0.028
1100	400	0.64	0.0007	0.028

Table 7

Findings from literature studies discussing the effect of TEMPO mediated oxidation on gas barrier properties compared to mechanical only treatments.

Reference	MFC production	Findings
Kumar et al. (2014)	MFC produced through TEMPO mediated oxidation and homogenizing compared to MFC produced through refining or refining followed by grinding in a Supermasscolloider.	OTR similar for different samples and WVTR lower for samples produced only mechanically.
Jiménez-López et al. (2020)	Refining followed by microfluidization or TEMPO oxidation followed by microfluidization.	TEMPO mediated oxidation did not result in lower WVTR compared to mechanical treatment only.
Chinga-Carrasco and Syverud (2012)	TEMPO mediated oxidation followed by homogenizing	TEMPO mediated oxidation decreased OTR compared to mechanical treatments only.
Bessonoff and Paltakari (2015)	TEMPO mediated oxidation followed by grinding compared to grinding with Supermasscolloider only	TEMPO mediated oxidation sample had similar OTR to mechanical only samples.
Fukuzumi et al. (2011)	TEMPO mediated oxidation MFC compared to a commercial mechanical only MFC	TEMPO mediated MFC sample had significantly lower OP.
Guivier et al. (2023)	MFC made through TEMPO mediated oxidation compared to MFC made through mechanical treatment only	Coatings of each sample had a similar OP.

Belbekhouche et al. (2011) when MFC films were found to have superior oxygen barrier properties to CNC films.

In contrast, the influence of TEMPO oxidation was also shown by Fukuzumi et al. (2011) where films or thin coatings of TEMPO oxidised MFC formed significantly better oxygen barriers than an MFC material with more coarse particles present. This result was also seen by Chinga-Carrasco and Syverud (2012) where a TEMPO mediated oxidation pre-treatment decreased OTR of films compared with mechanical only MFC. Possibly the difference in findings between these studies and those discussed previously was linked to the extent of delamination of the mechanical only treated samples. If large fibre fragments were present in the mechanical only treated samples used in these studies, this could cause defects in the film and reduce the ability for the MFC to form a gas barrier, as seen by Herrera et al. (2018).

5.2.2. The effect of carboxymethylation or enzyme pre-treatment on barrier properties of MFC

Studies discussing the use of a carboxymethylation or enzyme pre-

Table 8

Findings from literature studies discussing the effect of carboxymethylation or enzyme treatments on gas barrier properties compared to mechanical only treatments.

Reference	MFC production	Findings
Yook et al. (2020)	MFC produced through Supermasscolloider only or MFC produced by carboxymethylation followed by Supermasscolloider.	WVTR similar for both coatings but MFC coatings with carboxymethylation pre-treatment had lower OTR.
Chinga-Carrasco et al. (2012)	Carboxymethylation followed by homogenization.	MFC films with carboxymethylation treatment had lower OP.
Zhang et al. (2021)	Grinding with Supermasscolloider with or without carboxymethylation pre-treatment.	Carboxymethylated MFC coated papers had higher WVTR than MFC coatings produced through mechanical treatment only.
Djafari Petroudy et al. (2015)	Refining and homogenization with or without an endoglucanase enzyme pre-treatment.	Enzyme pre-treatment reduced OTR of MFC films.

treatment prior to a mechanical fibrillation stage as a way to improve barrier properties are summarised in Table 8.

The effect of carboxymethylation pre-treatment on the barrier properties of MFC coated paper or cardboard was evaluated by Yook et al. (2020) and Zhang et al. (2021). Yook et al. (2020) found that an MFC sample made through carboxymethylation followed by grinding in a Supermasscolloider produced coatings with lower OTR and similar WVTR to MFC made through mechanical only treatments. The authors suggested this was due to the smaller diameter of the carboxymethylated samples viewed in SEM images of the MFC coated paper leading to a more dense network that could prevent the transport of oxygen. However, the carboxymethylated MFC coatings had similar WVTR values to the mechanical only MFC coatings. Yook et al. (2020) suggested that the hydrophilic nature of the cellulose meant that increasing density of the MFC layer did not reduce WVTR values. Similarly, Zhang et al. (2021) found that an MFC sample made with a carboxymethylation pre-treatment had a higher WVTR than an MFC produced through mechanical treatment only. Air permeability of the carboxymethylated sample was lower, suggesting the carboxymethylated MFC formed a denser coating layer. This suggests the carboxymethylation reaction could have increased the interaction between cellulose and water and therefore, despite a more fibrillated MFC sample, the barrier properties to water vapour did not improve.

Chinga-Carrasco et al. (2012) studied how carboxymethylation of cellulose fibres prior to homogenization affected the oxygen barrier properties of MFC films. A lower oxygen transmission rate was measured for carboxymethylated MFC. This was thought to be due to the higher proportion of nano sized fibres and fewer large fibre aggregates observed in SEM images of the MFC films. This agrees with the results from Yook et al. (2020) and implies that the reduction in fibril size resulting from the carboxymethylation pre-treatment can result in a network of fibrils with increased tortuosity of the pore connectivity and therefore slow the transport of oxygen gas.

The research of Chinga-Carrasco et al. (2012) and Yook et al. (2020) suggest that an increased degree of fibril separation through a carboxymethylation pre-treatment can be useful to improve oxygen barrier if the MFC produced through mechanical treatment only is not fine enough to form a film with no connecting porosity. Padberg et al. (2016) suggests that this chemical pre-treatment is not necessary to form an MFC film with optimum oxygen barrier properties. However, a study directly comparing untreated and carboxymethylated pulp fibrillated using identical increasing fibrillation stages would be needed to properly address this question.

Using enzymes instead of carboxymethylation to produce finer MFC, Djafari Petroudy et al. (2015) studied the effect of an endoglucanase enzyme pre-treatment on the degree of fibrillation and oxygen barrier properties of MFC films made from bleached bagasse pulp. MFC was made through refining followed by homogenization. Films made from the enzyme pre-treated MFC had a lower oxygen permeability than those made through mechanical treatments only. The authors suggested this may be due to the smaller fibril diameter and narrower size distribution of the enzyme pre-treated samples. Therefore, adding an enzyme pre-treatment to improve fibrillation of MFC and therefore improve oxygen barrier properties may offer a more environmentally friendly alternative to carboxymethylation.

5.3. Increasing the intensity of a chemical pre-treatment

Several articles summarised in Table 9 have investigated the effect of increasing the intensity of a chemical pre-treatment prior to a mechanical fibrillation or disintegration stage.

A study by Wu et al. (2017) used a TEMPO mediated oxidation pre-treatment to produce MFC where the degree of fibrillation was altered by increasing the concentration of NaClO before homogenization which increased the cellulose carboxylate content from 0.5 to 1.8 mmol g⁻¹. This increase in carboxyl content increased fibril surface charge,

Table 9

Findings from literature studies increasing the intensity of a chemical pre-treatment.

Reference	MFC production	Findings
Sirvio et al. (2020)	Swelling cellulose fibres using deep eutectic solvent at different temperatures before microfluidizing.	Increasing temperature or treatment time decreases OP of MFC films.
Wu et al. (2017)	TEMPO oxidation with increasing amounts of NaClO added before homogenization	OP decreases as carboxylate content of cellulose increases.
Rodionova et al. (2012)	TEMPO oxidation with increasing carboxylation through either increasing reaction time or increasing NaClO concentration.	Increased cellulose carboxyl content decreased OTR of thin MFC films.
Ru et al. (2019)	Increasing the quaternary amine content of cellulose prior to homogenizing	Increased quaternary ammonium content increased OP.
Kubo et al. (2019)	TEMPO mediated oxidation or TEMPO mediated oxidation followed by mixing $Et_4N(OH)$. After homogenizing, $Et_4N(OH)$ modified cellulose was mixed into TEMPO oxidised cellulose suspensions at increasing ratios.	Increasing NEt_4^+ content of cellulose increased WVP and OP.
Naderi, Lindstrom, Flodberg, et al. (2016)	Phosphorylation followed by microfluidizing	Effect of increasing phosphorylation depended on RH and on number of passes through microfluidizer.
Gorur et al. (2020)	TEMPO mediated oxidation followed by periodate oxidation. Sheets made and fibrillated by increasing pH to 12.	Immersion in pH 12 solution before drying led to decreased OP.
Larsson et al. (2013)	Increasing degree of periodate oxidation followed by refining and microfluidizing.	Increasing periodate oxidation increased OP and WVP at 50 % RH but OP and WVP of periodate modified samples were lower at 80 % RH.

therefore increasing electrostatic repulsion and helping fibrils to separate. Oxygen transmission rate was lower for thin films of high carboxylate content MFC on a PLA substrate. Similarly, Rodionova et al. (2012) increased the cellulose carboxyl content from 0.4 to 1.4 mmol g^{-1} during TEMPO mediated oxidation through either increasing NaClO concentration or increasing the reaction time. Rodionova et al. (2012) also found a reduction in oxygen transmission rate of thin films of MFC coated onto PET as the reaction time or concentration of NaClO increased. Both studies linked the decrease in oxygen transmission to smaller fibril diameters or decreased number of fibre fragments as a result of increased electrostatic repulsion between fibrils during the mechanical disintegration phase caused by the increased number of carboxylate groups. Saito et al. (2007) found that a carboxyl content of 1.5 mmol g^{-1} corresponded to the oxidation of the C6 hydroxyl group to a carboxyl group on every second glucose unit on the external surface of the 3–4 nm diameter microfibrils. Possibly the increased NaClO concentration used by Wu et al. (2017) (2–10 mmol/ g of cellulose) compared to Saito et al. (2007) (1.3–5 mmol/ g of cellulose) could have led to oxidation of hydroxyl groups within the fibrils.

A different approach to increasing the degree of fibrillation was used by Sirvio et al. (2020) who used a deep eutectic solvent made of choline chloride and imidazole to treat cellulose fibres at increasing temperatures before microfluidization to increase swelling of the cellulose fibres and allow easier fibrillation into MFC. The research showed that fibres treated at increasing temperatures had smaller fibril diameters due to higher swelling in the pre-treatment phase and films made from these materials had lower oxygen permeability. This is further evidence that increasing the intensity of chemical treatments meant to help separate

fibrils results in a decreased fibril width which then leads to lower oxygen permeability of films.

In contrast to the above results, Larsson et al. (2013) increased the degree of periodate oxidation of cellulose by increasing reaction time prior to fibrillating by refining followed by microfluidizing. This led to an increase in oxygen and water vapour permeability at 50 % RH as the dialdehyde cellulose content increased. The authors linked this to a significant decrease in the degree of cellulose crystallinity resulting from the periodate oxidation process. Furthermore, a fibrillar structure was not visible in SEM images of films made from MFC with the highest dialdehyde cellulose content, suggesting that severe degradation of the cellulose had taken place. However, at 80 % RH, the WVP and OP of periodate oxidised MFC was lower than that of untreated MFC. The authors suggested that the cross linking between dialdehyde cellulose units was important in preventing swelling at high humidity and therefore maintaining barrier properties. This research shows that maintaining crystallinity and cellulose structure can be beneficial to barrier properties but these effects can be less significant at high RH than the benefits of decreasing moisture sensitivity of cellulose.

An innovative method to produce an MFC film was used by Gorur et al. (2020) through performing TEMPO mediated oxidation on cellulose followed by periodate oxidation, forming a sheet through vacuum filtration and then increasing the pH to introduce charges, break hemiacetal links and fibrillate the fibres. A reaction scheme is shown in Fig. 8 and the results are summarised in Table 10. A substantial decrease in oxygen permeability was seen for the sheets immersed in pH 12 solution before drying compared to sheets made without this stage. This was due to the extensive fibrillation of the cellulose compared to the pre-treated pulp fibres in their uncharged form. The increased fibrillation was clearly visible in SEM images of the film surfaces. Despite increased charge on the cellulose and breakage of the hemiacetal cross linkages caused by increasing the pH, the OP was still lower for the fibrillated samples at 80 % humidity. This result was different from that of Larsson et al. (2013), who found that cross linkages from periodate oxidation likely prevented swelling at high humidity and helped to maintain barrier properties. This could be because the degree of fibrillation of the samples was very different in the case of Gorur et al. (2020) so the difference in density of the film had more of an effect on the transmission of oxygen than the increase in swelling from breaking the cross linkages.

Similar to Rodionova et al. (2012) and Wu et al. (2017), Naderi, Lindstrom, Flodberg, et al. (2016) increased the intensity of a chemical pre-treatment but achieved this using a phosphorylation reaction rather than carboxylation to add negatively charged groups to cellulose fibres in order to increase separation into fibrils via increased electrostatic repulsion. Naderi, Lindstrom, Flodberg, et al. (2016) found that when the degree of substitution of the phosphate group on cellulose increased, the resulting effect on the oxygen permeability of MFC films made from the phosphorylated cellulose was complex. For example, samples made with only one pass through the microfluidizer showed an initial decrease in OP as degree of substitution increased followed by an increase in OP after a further increase in degree of substitution. For samples made from 2 passes through the microfluidizer, increasing phosphorylation decreased OP- particularly for the measurements at 80 % RH. There was an increased nanofraction measured through centrifugation as the degree of substitution increased due to the negative charges on the phosphate groups aiding fibrillation. Potentially after only one pass through the microfluidizer, the fibrillation was relatively low and the network was not strong enough to prevent swelling in the increased RH during oxygen barrier testing. Increasing the cellulose charge by increasing the degree of substitution may not have had a negative impact on oxygen barrier for more fibrillated samples because maybe the high degree of fibrillation had a higher impact, similar to what was reported by Gorur et al. (2020).

Conversely, there has also been research into increasing the intensity of positive charge on functionalised cellulose with the aim to improve

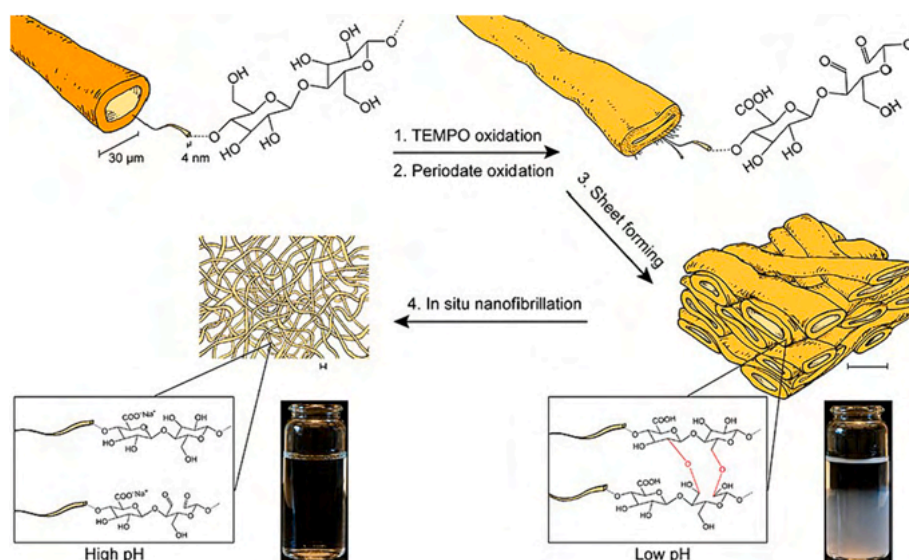


Fig. 8. Reaction scheme for TEMPO mediated oxidation of cellulose followed by periodate oxidation followed by increasing pH to 12 (unmodified from original). From Gorur YC, Larsson PA, Wågberg L (2020) Correction to “self-fibrillating cellulose fibres: Rapid in situ nanofibrillation to prepare strong, transparent, and gas barrier nanopapers”. *Biomacromolecules* 21(8):3479–3479, <https://doi.org/10.1021/acs.biomac.0c00997>, Copyright © 2020 American Chemical Society, with CC-BY, license information and disclaimer or warranties available at: <https://creativecommons.org/licenses/by/4.0/legalcode>.

Table 10

Effect of the fibrillation process described by Gorur et al. (2020) on measurements of oxygen permeability of MFC films.

	Oxygen permeability at 50 % RH ($\text{cm}^3 \mu\text{m m}^{-2} \text{d}^{-1} \text{kPa}^{-1}$) % RH	Oxygen permeability at 80 % RH ($\text{cm}^3 \mu\text{m m}^{-2} \text{d}^{-1} \text{kPa}^{-1}$)
Unfibrillated	1.6	8.4
Fibrillated	0.7	2.4

barrier properties of MFC films. Ru et al. (2019) produced MFC from bamboo pulp by adding a quaternary amine group with increasing degree of substitution to cellulose and therefore increasing positive charge prior to homogenizing. Increasing positive charge initially decreased the oxygen transmission rate of thin layers of MFC coated onto PLA, but further increasing the charge increased the oxygen transmission rate despite the higher charged MFC having a smaller fibril diameter. The authors suggested that this could be linked to the decrease in density of films as the cellulose charge content increased since the quaternary amine groups are not able to take part in the hydrogen bonding between fibrils and the methyl groups around the nitrogen provide significant steric hindrance which could prevent other hydrogen bonding interactions between available hydroxyl groups and reduce close packing of the cellulose. This decrease in bonding through the large bulky amine group prevented increasing the degree of fibrillation of cellulose from improving barrier properties. Similarly, Kubo et al. (2019) mixed TEMPO oxidised MFC with increasing amounts of MFC produced by adding $\text{Et}_4\text{N}(\text{OH})$ after TEMPO mediated oxidation prior to homogenizing. Film density decreased as the molar ratio of Et_4N^+ increased. This corresponded with an increase in both oxygen and water vapour permeability. The authors suggested that the bulky alkyl groups introduced steric hindrance and may have weaker intermolecular forces than the hydrogen bonds present between carboxyl groups in TEMPO oxidised cellulose. The studies of Ru et al. (2019) and Kubo et al. (2019) showed that there can be unintentional changes to the structure of MFC networks as a result of functionalising the cellulose to introduce electrostatic charges. If the functional group added to the cellulose provides sufficient steric hindrance, it may interfere with hydrogen bonding between and close packing of the cellulose fibrils which could have a larger impact than decreasing fibril diameter. Potentially the conflicting results seen by Naderi, Lindstrom, Flodberg, et al. (2016) could also have

been influenced by steric hindrance from the phosphate groups preventing close packing of fibrils and therefore leading to some increases in OP as the degree of phosphate substitution increased.

5.4. Comparisons of different pre-treatments

5.4.1. Comparison of Carboxymethylation with other pre-treatments

Research into the effects of carboxymethylation compared to other pre-treatments aiming to increase the degree of fibrillation of cellulose is summarised in Table 11.

The studies of Minelli et al. (2010) and Plackett et al. (2010)

Table 11

Findings from literature studies comparing enzyme and carboxymethylation pre-treatments.

Reference	MFC production method	Findings.
Minelli et al. (2010)	Compared carboxymethylation with enzyme treatment and refining as pre-treatments to homogenizing.	WVP higher but OP lower for enzyme treated sample
Plackett et al. (2010)	Carboxymethylation compared with enzyme treatment and refining as pre-treatments to homogenizing.	No significant difference in OP between samples when considering variation.
Naderi, Lindstrom, Sundstrom, et al. (2016)	Compared enzyme treatment and refining, carboxymethylation and the grafting of carboxymethyl cellulose all before microfluidization.	CMC modified sample had higher OP than enzyme treated and carboxymethylated.
Fall et al. (2022)	Carboxymethylation or enzyme pre-treatment followed by microfluidizing	Carboxymethylated MFC films had lowest OP.
Naderi, Larsson, et al. (2017)	Compared alkoxylation with a carboxymethyl group with a carboxyethyl group before microfluidizing.	MFC modified with carboxyethyl group had higher OP.
Naderi, Koschella, et al. (2017)	Carboxymethylation or sulfoethylation followed by microfluidization	Carboxymethylated sample had lower OP.
Naderi, Lindstrom, Flodberg, et al. (2016)	Carboxymethylation or phosphorylation prior to microfluidizing	Both pre-treatment stages produced MFC films with similar OP values.

compared oxygen permeability of MFC films made from a carboxymethylation or enzyme treatment each followed by homogenization. Plackett et al. (2010) found no significant difference in oxygen permeability between the two types of MFC films. The authors suggested that although the fibril diameter of the carboxylated MFC was lower, it contained large fibre fragments which may have disrupted the MFC network. However, Minelli et al. (2010) found that the films made from enzyme treated MFC had lower oxygen permeability and a higher density. In spite of the lower oxygen permeability, the authors measured lower oxygen diffusivity in the carboxymethylated MFC films. The measurement of oxygen diffusivity is not common so it is difficult to compare this to other studies. Minelli et al. (2010) also found that the water vapour permeability and diffusivity was lower for the carboxymethylated samples, which was thought to be because this MFC had smaller fibril diameter and a narrower size distribution which led to higher tortuosity in the gas diffusion path. A study by Fall et al. (2022) also compared an enzyme pre-treatment with a carboxymethylation pre-treatment prior to microfluidization. The authors found that the carboxymethylated MFC had the finest structure from AFM imaging along with the highest light transmittance solution and highest viscosity, all indications that this sample had the highest degree of fibrillation. As expected from the higher degree of fibrillation, the carboxymethylated MFC films had the lowest oxygen permeability. This contrasts with the results from Plackett et al. (2010) which found no significant differences in OP between MFC films produced from carboxymethylated and enzyme treated MFC. An investigation by Naderi, Lindstrom, Sundstrom, et al. (2016) also compared enzyme treated with carboxymethylated MFC with the additional comparison point of MFC produced with a CMC grafting pre-treatment. In all cases, microfluidization was used as the mechanical disintegration step. The carboxymethylated MFC had a higher percentage of nano sized fraction measured by the solids content of the supernatant after centrifuging, but the enzyme pre-treated MFC had the lowest oxygen permeability, agreeing with the results seen by Minelli et al. (2010).

Naderi, Lindstrom, Sundstrom, et al. (2016) suggested that the differences in oxygen permeability between films made from MFC produced through different methods could be due to the higher surface charge on the carboxymethylated MFC sample leading to stronger interaction with water vapour during the oxygen transmission rate test. Since the test was performed at 50 % relative humidity, there would have been some moisture present in the testing chamber which could

adsorb to the cellulose. In fact, Meriçer et al. (2017) measured moisture vapour adsorption isotherms of the MFC films and found that the films produced from carboxymethylated MFC sorbed more moisture vapour due to the higher surface charge. The additional sorbed moisture vapour can increase swelling of the film. A higher water sorption for the carboxymethylated MFC film was also seen by Minelli et al. (2010). Fig. 9 shows that there is a significant increase in oxygen permeability between 0 and 0.5 water activity (corresponding to 0 % and 50 % RH). Variation in the results is too large to conclude that carboxymethylated MFC OP increases differently than enzyme treated MFC with changing RH. However, water sorption data clearly showed that water sorption was higher for carboxymethylated MFC.

The potential detrimental effect of surface charge on oxygen permeability was also seen by Naderi, Larsson, et al. (2017) where the authors used an alkoxylation treatment using firstly the standard monochloro acetic acid (MCA) to produce a carboxymethylation reaction and then used 2-chloro propionic (CPA) acid to increase the size of the charged groups added to the cellulose fibres. The use of the CPA reagent resulted in a higher fraction of nano sized cellulose fragments and higher viscosity suspensions. However, the oxygen permeability of the MCA treated MFC was lower than the CPA treated MFC. The authors suggested this was due to the oxygen permeability testing taking place under 50 % or 80 % relative humidity and the fact that the surface charge and water retention values were higher for the CPA treated MFC. Therefore, this may have led to a stronger interaction with water vapour, causing swelling of the film and disruption of the network which allowed higher transmission of oxygen. This agrees with the results seen in Naderi, Lindstrom, Sundstrom, et al. (2016) where a more highly charged MFC sample made films with higher oxygen permeability despite a higher degree of fibrillation. However, the decreased OP for the MFC with the larger size alkoxy group seen by Naderi, Larsson, et al. (2017) could also be due to increased steric hindrance from the bulkier group preventing close packing of the fibrils, as seen by Ru et al. (2019).

Naderi, Koschella, et al. (2017) and Naderi, Lindstrom, Flodberg, et al. (2016) compared sulfoethylation or phosphorylation to carboxymethylation of cellulose as a pre-treatment to microfluidizing. Naderi, Lindstrom, Flodberg, et al. (2016) found that carboxymethylated MFC formed films with a similar OP to phosphorylated samples. However, Naderi, Koschella, et al. (2017) found that the sulfoethylated MFC formed films with higher OP than the carboxymethylated sample despite having a higher percentage of nanofraction fines measured through

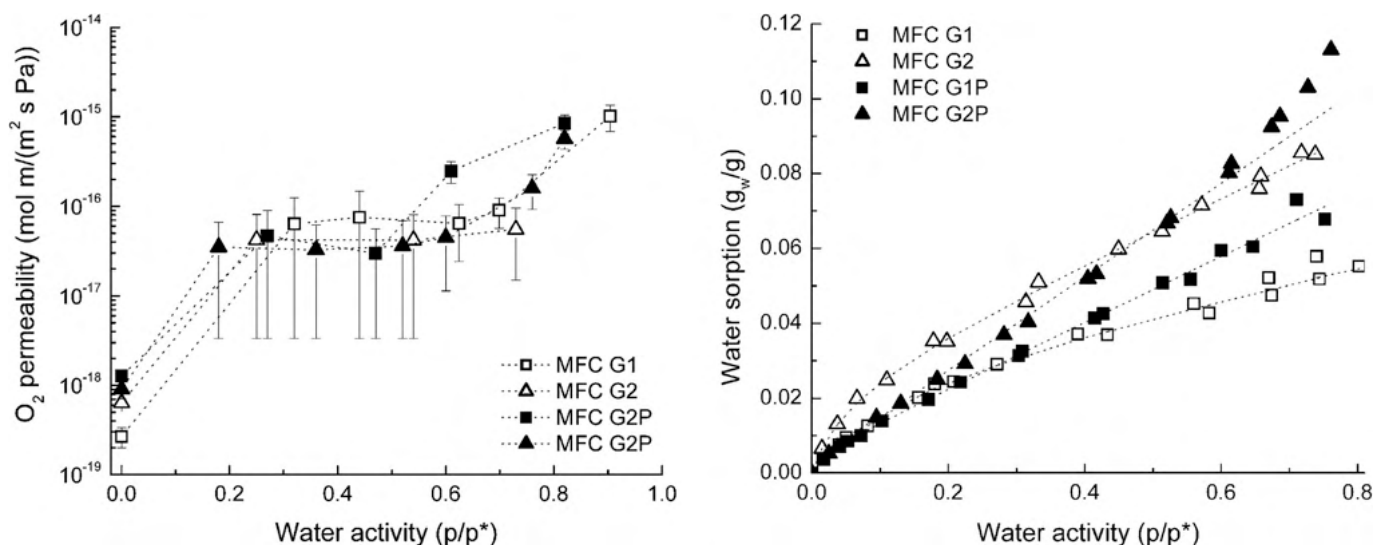


Fig. 9. Variation in water sorption and oxygen permeability with increasing water activity for MFC films. MFC G1 refers to MFC made through enzyme treatment and refining followed by homogenizing and MFC G2 refers to MFC made by carboxymethylation followed by homogenizing. G1P and G2P refer to plasticized versions of the same MFC samples. Reprinted from: Journal of Membrane Science, 358 (1–2), M. Minelli, M. Giacinti Baschetti, F. Doghieri, M. Ankerfors, T Lindström, I. Siró, D. Plackett, Investigation of mass transport properties of microfibrillated cellulose (MFC) films, 67–75, Copyright (2010), with permission from Elsevier.

centrifugation. The viscosity of sulfoethylated MFC suspensions were also higher than carboxymethylated samples, further suggesting a higher degree of fibrillation for the sulfoethylated MFC. However, AFM images showed that fibril length and width for the two samples were similar. The authors suggested that the sulfoethylated MFC may have been more prone to swelling and this could be why the OP was higher at 50 % and 80 % RH. Steric hindrance from the large sulfoethyl groups may also have contributed to a lower OP.

6. Discussion

Literature studies looking at how MFC pre-treatments affect gas barrier properties have varying results. There is no straightforward relationship between increasing degree of fibrillation of MFC, through either increased mechanical processing or adding a chemical pre-treatment, and improving gas barrier properties. For samples where only mechanical treatments were used, increasing the intensity of the mechanical treatment can improve gas barrier properties but there is a plateau in this effect. This was seen by Juntunen (2021), Padberg et al. (2016), and Wei et al. (2023). Once the MFC network has no connecting porosity, further fibrillating the cellulose may not show any benefit to gas barrier properties (Padberg et al., 2016). For samples with a chemical or enzyme pre-treatment, increasing mechanical processing may not improve gas barrier properties because the MFC network can already be dense enough that increasing fibrillation does not further reduce gas transport (Aulin et al., 2010). This effect was seen by Aulin et al. (2010) and Siró et al. (2011). In fact, applying too much mechanical treatment can be detrimental to barrier properties by reducing length and crystallinity of fibrils, an effect seen by Fukuzumi et al. (2013).

Increasing the degree of fibrillation by increasing the intensity of a chemical pre-treatment can be effective in improving barrier properties. For example, Rodionova et al. (2012) and Wu et al. (2017) found that increasing intensity of TEMPO mediated oxidation reduced oxygen permeability of MFC films. However, if the chemical pre-treatment involves adding bulky groups, this may be detrimental to close packing of fibrils due to steric hindrance, as seen by Ru et al. (2019). Furthermore, chemical pre-treatments often introduce negative charges to help fibrillate the cellulose and these negative charges can lead to stronger interactions with water vapour, therefore increasing WVP or decreasing OP at high RH. This effect was suspected by Naderi, Lindstrom, Sundstrom, et al. (2016) when an enzyme treated sample with a supposedly lower degree of fibrillation than a carboxymethylated formed better oxygen barriers at 50 % RH. For this reason, chemical pre-treatments that act to reduce swelling such as periodate oxidation were found by Larsson et al. (2013) to be most effective at reducing oxygen permeability at high relative humidity. However, using a periodate oxidation reaction with a high rate of conversion can lead to a decrease in barrier performance, potentially due to a decrease in cellulose crystallinity as seen by Larsson et al. (2013).

Cellulose crystallinity may have some influence on the barrier properties of MFC films but this appears to be a less important effect than fibrillation. If pre-treatments reduce crystallinity but increase fibrillation, the gas barrier properties may still improve or remain constant. This effect was seen by Padberg et al. (2016) and Siró et al. (2011) and Wei et al. (2023). However, if crystallinity is decreased without a significant increase in fibrillation, Larsson et al. (2013) showed that this may have a negative effect on barrier properties. It is difficult to precisely understand how the crystallinity of MFC affects the gas barrier properties of films and coatings because processes that alter the crystallinity of the cellulose also often change the morphology of the material. Furthermore, it is difficult to quantitatively compare crystallinity index of cellulose materials (Park et al., 2010).

The source of the cellulose used to make the MFC may also have some influence on how degree of fibrillation relates to barrier properties. For example, Kumar et al. (2014) found that there were differences

in OTR between MFC films made from hardwood and softwood pulp. In addition, Yook et al. (2020) found that unbleached kraft pulp formed a less effective barrier to oxygen than bleached kraft pulp under the same fibrillation conditions, suggested to be because the unbleached MFC had larger fibril diameters. Rodionova et al. (2012) treated both spruce and eucalyptus pulp with TEMPO mediated oxidation followed by homogenization and found that the spruce based MFC formed films with lower OTR than the eucalyptus based MFC after the same chemical and mechanical treatments on the cellulose. Therefore, pulp type or cellulose source may influence the effect of fibrillation on barrier because different pulp types may reach a different degree of fibrillation under fixed chemical or mechanical conditions. For example, Maliha et al. (2022) found that the WVTR of films made from bleached eucalyptus kraft pulp was lower than that of bleached pine pulp when the material had been processed in the same way, possibly due to less efficient fibrillation of the longer, thicker pine fibres. The cellulose source may also affect the crystallinity and degree of polymerisation of the cellulose which may influence the barrier properties. Therefore, another factor complicating the relationship between degree of fibrillation and gas barrier properties may be the use of different pulp types.

In many cases in this review, it has been difficult to conclusively state whether increasing fibrillation has an effect on barrier properties because variation in the oxygen barrier results can be greater than the difference in OTR or OP between samples. This may imply that in these cases the increased fibrillation does not have a significant effect on barrier properties. However, other factors can influence this variation. For example, defects in films or coatings such as pinholes or cracks can allow gas transmission (da Silva Sobrinho et al., 2000). These defects may have more of an effect on the rate of oxygen diffusion through the cellulose network than changes in cellulose characteristics and can contribute to high standard deviations in the results.

7. Conclusion

Increasing the degree of fibrillation of MFC by increasing mechanical processing or the addition of a chemical or enzyme pre-treatment can be an effective way to improve gas barrier properties. However, there are varying effects from different chemical pre-treatments that may be detrimental to barrier properties, for example increasing swelling by introducing charges or introducing groups with large steric size which prevent fibrils packing closely together. There is a delicate balance between improving the barrier properties of MFC films or coatings by deliberately improving the separation of fibrils from fibres and avoiding factors which may be detrimental to barrier properties such as increasing moisture sensitivity from the addition of charged groups, decreasing cellulose crystallinity or decreasing fibril length or degree of polymerisation. The issue of decreasing barrier properties at high relative humidity requires further research and consideration to make the use of MFC films in sustainable food packaging applications successful.

CRediT authorship contribution statement

Robyn Hill: Writing – review & editing, Writing – original draft, Investigation. **Jon Phipps:** Writing – review & editing, Supervision. **Richard Greenwood:** Writing – review & editing, Supervision, Funding acquisition. **David Skuse:** Writing – review & editing, Supervision. **Zhenyu Jason Zhang:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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This code was written to calculate the wavelength exponent of MFC coatings on a paper substrate. Ro refers to the measurement of the reflectivity of one MFC coated sheet over a black background. Roo refers to the measurement of the reflectivity of one MFC coated sheet over a stack of 10 base sheets. The reference Ro and Roo refer to one base sheet over a black background and a stack of base sheets over a black background.

The Kubelka-Munk approximation is used to calculate the S and K of the MFC layer from this data, followed by creating plots of LogS vs Logwavelength which were used to calculate a wavelength exponent for the MFC coating (ref G. Kortum, Reflectance Spectroscopy, Springer-Verlag, Germany, 1969)

The steps that are needed for this analysis to work are:

. Read both the Ro and Roo measurements into Python and index by the wavelength . Read reference Ro and Roo into Python and index by the wavelength . Read in the equations needed to calculate S and K for the MFC layer using the Kubelka-Munk approximation . Calculate LogS for each measurement for each wavelength . Plot LogS against Logwavelength for each measurement . Calculate the slope and Rsquared of LogS as a function of Logwavelength for each measurement and output to csv . Calculate average slope and Rsquared for each MFC sample

```
In [1]: import warnings
warnings.simplefilter('ignore', FutureWarning)

import matplotlib
#matplotlib.rcParams['axes.grid'] = True
%matplotlib inline
import csv
from pandas import *
import pandas as pd
```

```
In [2]: #https://stackoverflow.com/questions/1810743/how-to-set-the-current-working-directo
import os
os.getcwd()
os.chdir("C:\\Users\\RobynHill\\OneDrive - FiberLean Technologies\\Big Pulp\\Light
```

```
In [3]: #First step is to read in csv files for Ro and Roo and check that the data is displ
Romeasured = read_csv('Romeasured.csv')
Romeasured.head()
Romeasured.index = Romeasured['wavelength']
Romeasured.head(2)
```

```
Out[3]:
```

	wavelength	U1-1	U1-2	U1-3	U1-4	U1-5	U1-6	U1-7	U1-8	U1-9	...
	wavelength										
	430	430	48.735	47.466	47.891	49.284	48.908	47.511	47.040	46.527	47.995 ...
	440	440	51.270	50.001	50.377	51.794	51.486	49.979	49.601	49.066	50.466 ...

2 rows × 301 columns

```
In [4]: Roomeasured = read_csv('Roomeasured.csv')
Roomeasured.head()
```

```
Roomeasured.index = Roomeasured['wavelength']
Roomeasured.head(2)
```

```
Out[4]:
```

	wavelength	U1-1	U1-2	U1-3	U1-4	U1-5	U1-6	U1-7	U1-8	U1-9	...	
	430	430	51.277	50.331	49.410	50.733	50.902	50.052	49.841	49.241	50.715	...
	440	440	54.317	53.456	52.569	53.842	53.995	53.155	52.998	52.400	53.863	...

2 rows × 301 columns

```
In [45]: #Need average Ro and Roo for each wavelength for the reference values (the base sheet)
Reference_mean = read_csv('Reference_mean_data.csv')
Reference_mean.head()
Reference_mean.index = Reference_mean['wavelength']
Reference_mean.head(2)
```

```
Out[45]:
```

	wavelength	Mean Ro	Reference	Mean Roo	reference
	430	430	80.778	86.632	
	440	440	81.377	88.123	

```
In [46]: # Divide Ro reference and Roo reference by 100 to be used in calculations.
# Add a parameter for Log10wavelength
#https://pythonforundergradengineers.com/exponents-and-logs-with-python.html

import numpy as np

def divideby100 (value):
    return (value/100)
RRO = 'Mean Ro Reference'
Reference_mean[RRO] = Reference_mean[RRO].apply(divideby100)
RROO = 'Mean Roo reference'
Reference_mean[RROO] = Reference_mean[RROO].apply(divideby100)
WAVELENGTH = 'wavelength'
Reference_mean["log10wavelength"] = np.log10(Reference_mean[WAVELENGTH])

Reference_mean.head()
```

```
Out[46]:
```

	wavelength	Mean Ro	Reference	Mean Roo	reference	log10wavelength
	430	430	0.80778	0.86632		2.633468
	440	440	0.81377	0.88123		2.643453
	450	450	0.81418	0.88592		2.653213
	460	460	0.81360	0.88710		2.662758
	470	470	0.81273	0.88713		2.672098

```
In [7]: # Kubelka-Munk approximation calculations for S and K
# Roreal is the true value of Ro for the MFC coating, RROO is the Roo of the base sheet
# R1 is the measured reflectance of an MFC coated sheet over a black background
# R2 is the measured reflectance of an MFC coated sheets over a stack of base sheet
```

```

# Rooreal is the true value of Roo for the MFC coatings
# S is the scattering coefficient given in cm^2/g, K is the absorption coefficient
# https://www.datasciencemadesimple.com/log-natural-logarithmic-value-column-pandas

import numpy as np

def Roreal(RROO,RRO,R1,R2):
    Roreal = (RROO*(R1/100)-(R2/100)*RRO)/((RROO*(R1/100)*RRO)-(RRO*(R2/100)*RROO)-
    return Roreal

def a(R1,Roreal,RRO):
    a = 0.5*((R1/100)+((Roreal-(R1/100)+RRO)/(Roreal*RRO)))
    return a

def b(a):
    b = ((a**2)-1)**0.5
    return b

def Roo(a,b):
    Rooreal = a-b
    return Rooreal

def S(b,Roreal,Rooreal):
    S = (1/(0.0006*2*b))*(np.log((1-Roreal*Rooreal)/(1-Roreal/Rooreal)))
    return S

def K(S,Rooreal):
    K = S*((1-Rooreal)**2)/(2*Rooreal))
    return (K)

```

```

In [8]: # Create a data frame in Python for the Roreal data to be stored
#https://www.tutorialspoint.com/how-to-create-a-dataframe-in-python
import pandas as pd
Roreals=pd.DataFrame()

```

```

In [9]: # Find number of columns in Romeasured to know how many iterations of calculation
len(Romeasured.columns)

```

```

Out[9]: 301

```

```

In [10]: #Calculate Roreal for each measurement of reflectance
#https://sparkbyexamples.com/pandas/pandas-iterate-over-columns-of-dataframe-to-run
#https://www.projectpro.io/recipes/append-output-of-for-loop-python-dataframe#:~:te
#https://stackoverflow.com/questions/62931809/cannot-concatenate-object-of-type-cla
#https://sparkbyexamples.com/pandas/pandas-iterate-over-columns-of-dataframe-to-run
# https://www.geeksforgeeks.org/different-ways-to-iterate-over-rows-in-pandas-dataf
# https://sparkbyexamples.com/pandas/iterate-over-rows-in-pandas-dataframe/#:~:text
#https://www.geeksforgeeks.org/loop-or-iterate-over-all-or-certain-columns-of-a-dat
for column in Romeasured.iloc[:301]:
    for column in Roomeasured.iloc[:301]:
        Roreals=Roreals.append(Roreal(Reference_mean[RROO], Reference_mean[RRO], Ro
    break
break

```

```

Input In [10]
break
^
SyntaxError: 'break' outside loop

```

```

In [38]: #Print results from the loop to assess
Roreals.head()

```

```
Out[38]: wavelength    430    440    450    460    470    480    490    500    5
0  4.300000  4.400000  4.500000  4.600000  4.700000  4.800000  4.900000  5.000000  5.1000
1  0.196208  0.214674  0.215302  0.210740  0.222812  0.213819  0.226159  0.223553  0.2163
2  0.120644  0.131548  0.139253  0.149515  0.143255  0.144296  0.147376  0.146605  0.1407
3  0.329058  0.312065  0.315250  0.311220  0.307008  0.301854  0.305908  0.308525  0.3038
4  0.354259  0.346277  0.336981  0.337105  0.329210  0.323302  0.319859  0.313291  0.3214
```

5 rows × 28 columns

```
In [39]: #Transpose data to give columns with same format as input data
#https://note.nkmk.me/en/python-pandas-t-transpose/#:~:text=Use%20the%20T%20attribu
Rorealstrans=Rorealstrans.T
Rorealstrans.head()
#del Rorealstrans[Rorealstrans.columns[0]]
```

```
Out[39]:      0      1      2      3      4      5      6      7      8
wavelength
430  4.3  0.196208  0.120644  0.329058  0.354259  0.280886  0.178792  0.126129  0.134364  0
440  4.4  0.214674  0.131548  0.312065  0.346277  0.289381  0.176136  0.134968  0.137053  0
450  4.5  0.215302  0.139253  0.315250  0.336981  0.276636  0.180407  0.135823  0.154849  0
460  4.6  0.210740  0.149515  0.311220  0.337105  0.271316  0.175001  0.141699  0.158533  0
470  4.7  0.222812  0.143255  0.307008  0.329210  0.273661  0.172091  0.137265  0.163213  0
```

5 rows × 301 columns

```
In [40]: #Change column titles to the column titles from the original data set. Add in a wav
#https://stackoverflow.com/questions/36846060/how-to-replace-an-entire-column-on-pa
Rorealstrans.columns=Romeasured.columns
Rorealstrans["wavelength"]=Romeasured["wavelength"]
Rorealstrans.head()
```

```
Out[40]:      wavelength  U1-1  U1-2  U1-3  U1-4  U1-5  U1-6  U1-7
wavelength
430      430  0.196208  0.120644  0.329058  0.354259  0.280886  0.178792  0.126129  0.1
440      440  0.214674  0.131548  0.312065  0.346277  0.289381  0.176136  0.134968  0.1
450      450  0.215302  0.139253  0.315250  0.336981  0.276636  0.180407  0.135823  0.1
460      460  0.210740  0.149515  0.311220  0.337105  0.271316  0.175001  0.141699  0.1
470      470  0.222812  0.143255  0.307008  0.329210  0.273661  0.172091  0.137265  0.1
```

5 rows × 301 columns

```
In [ ]: #Export Rorealstrans to csv
#https://towardsdatascience.com/how-to-export-pandas-dataframe-to-csv-2038e43d9c03
Rorealstrans.to_csv("Rorealstrans.csv")
```

```
In [16]: #Create data frame for A values
As=pd.DataFrame()
```

```
In [17]: #Calculate A values
for column in Romeasured.iloc[:301]:
    for column in Roomeasured.iloc[:301]:
        As=As.append(a(Romeasured[column], Rorealstrans[column], Reference_mean[RRC
    break
break
```

Input In [17]
break
^
SyntaxError: 'break' outside loop

```
In [41]: #Transpose A values, change column titles and add in wavelength column, print data
Astrans=As.T
Astrans.columns=Romeasured.columns
Astrans["wavelength"]=Romeasured["wavelength"]
Astrans.head()
```

```
Out[41]:
```

	wavelength	U1-1	U1-2	U1-3	U1-4	U1-5	U1-6	U1-7	
wavelength									
430	430	1.873522	2.565424	1.477062	1.415681	1.565830	2.008242	2.509880	2.4
440	440	1.732473	2.329919	1.476667	1.398307	1.506510	1.959594	2.308986	2.3
450	450	1.680070	2.164864	1.438684	1.385382	1.500432	1.871220	2.215125	2.0
460	460	1.650327	2.002563	1.416192	1.359202	1.477820	1.842076	2.082140	1.9
470	470	1.568293	1.983260	1.396376	1.346995	1.442057	1.803496	2.049863	1.8

5 rows × 301 columns

```
In [ ]: #Export A values to csv
Astrans.to_csv("Astrans.csv")
```

```
In [20]: #Calculate B values
Bs=pd.DataFrame()
for column in Astrans.iloc[:301]:
    Bs=Bs.append(b(Astrans[column]),ignore_index=True)#,index=Reference_mean["wavel
```

```
In [21]: # Transpose Bs, rename columns and add wavelength column. Print to check the Loop k
Bstrans=Bs.T
Bstrans.columns=Astrans.columns
Bstrans["wavelength"]=Romeasured["wavelength"]
Bstrans.head()
Bstrans.to_csv("Bstrans.csv")
```

Out[21]:

	wavelength	U1-1	U1-2	U1-3	U1-4	U1-5	U1-6	U1-7
	wavelength							
430	430	1.584324	2.362499	1.087065	1.002074	1.204916	1.741561	2.302064
440	440	1.414731	2.104406	1.086530	0.977375	1.126753	1.685233	2.081206
450	450	1.350051	1.920062	1.034317	0.958792	1.118614	1.581601	1.976557
460	460	1.312852	1.735010	1.002795	0.920560	1.088096	1.547011	1.826282
470	470	1.208115	1.712694	0.974610	0.902439	1.039004	1.500866	1.789396

5 rows × 301 columns

In [23]:

```
#Calculation of Rooreal for MFC Layers and print to csv
Rooreals=Astrans*Bstrans
Rooreals["wavelength"]=Romeasured["wavelength"]
Rooreals.head()
Rooreals.to_csv("Rooreals.csv")
```

Out[23]:

	wavelength	U1-1	U1-2	U1-3	U1-4	U1-5	U1-6	U1-7
	wavelength							
430	430	0.289197	0.202925	0.389996	0.413607	0.360914	0.266681	0.207816
440	440	0.317742	0.225513	0.390138	0.420932	0.379757	0.274361	0.227780
450	450	0.330020	0.244802	0.404367	0.426590	0.381818	0.289618	0.238568
460	460	0.337475	0.267553	0.413396	0.438642	0.389724	0.295065	0.255858
470	470	0.360178	0.270566	0.421765	0.444556	0.403053	0.302630	0.260467

5 rows × 301 columns

In [24]:

```
#Calculate S for each measurement of MFC Ro and Roo
#https://www.prepbytes.com/blog/python/iloc-function-in-python/#:~:text=The%20iloc%
Ss=pd.DataFrame()
for column in Bstrans.iloc[:, 1:301]:
    for column in Rorealstrans.iloc[:, 1:301]:
        for column in Rooreals.iloc[:, 1:301]:
            Ss=Ss.append(S(Bstrans[column], Rorealstrans[column], Rooreals[column]))
        break
    break
break
```

```
C:\Users\RobynHill\anaconda3\lib\site-packages\pandas\core\arraylike.py:397: RuntimeWarning: invalid value encountered in log
  result = getattr(ufunc, method)(*inputs, **kwargs)
C:\Users\RobynHill\anaconda3\lib\site-packages\pandas\core\arraylike.py:397: RuntimeWarning: invalid value encountered in log
  result = getattr(ufunc, method)(*inputs, **kwargs)
C:\Users\RobynHill\anaconda3\lib\site-packages\pandas\core\arraylike.py:397: RuntimeWarning: invalid value encountered in log
  result = getattr(ufunc, method)(*inputs, **kwargs)
C:\Users\RobynHill\anaconda3\lib\site-packages\pandas\core\arraylike.py:397: RuntimeWarning: invalid value encountered in log
  result = getattr(ufunc, method)(*inputs, **kwargs)
C:\Users\RobynHill\anaconda3\lib\site-packages\pandas\core\arraylike.py:397: RuntimeWarning: invalid value encountered in log
  result = getattr(ufunc, method)(*inputs, **kwargs)
```

Input In [24]

```
break
```

^

SyntaxError: 'break' outside loop

```
In [25]: #Transpose S values, add the wavelength column and change the column names, print to
#https://discuss.codecademy.com/t/can-we-add-a-new-column-at-a-specific-position-in
Sstrans=Ss.T
Sstrans.insert(0, 'wavelength', Romeasured["wavelength"].values)
Sstrans.columns=Astrans.columns
Sstrans.head()
Sstrans.to_csv("Sstrans.csv")
```

```
Out[25]:
```

	wavelength	U1-1	U1-2	U1-3	U1-4	U1-5	U1-6
wavelength							
430	430	566.069920	309.668975	1317.717314	1482.808982	967.825954	507.748326
440	440	621.557151	334.747722	1134.374445	1340.371367	975.621112	483.437387
450	450	606.752917	350.068293	1108.630895	1221.304195	877.287909	485.593270
460	460	574.841986	373.428562	1047.064485	1179.753052	826.782528	455.798997
470	470	607.207996	347.575365	994.375487	1099.707824	817.569672	437.165203

5 rows × 301 columns

```
In [26]: # Calculate K values
Ks=pd.DataFrame()
for column in Sstrans.iloc[:301]:
    for column in Rooreals.iloc[:301]:
        Ks=Ks.append(K(Sstrans[column], Rooreals[column]),ignore_index=True)#,index=
    break
break
```

Input In [26]

```
break
```

^

SyntaxError: 'break' outside loop

```
In [27]: # Transpose K values, rename columns, add in wavelength column, print to check, and
Kstrans=Ks.T
Kstrans.columns=Astrans.columns
Kstrans["wavelength"]=Romeasured["wavelength"]
```

```
Kstrans.head()
#Kstrans.to_csv("Kstrans.csv")
```

Out[27]:

	wavelength	U1-1	U1-2	U1-3	U1-4	U1-5	U1-6
wavelength							
430	430	494.474433	484.763297	628.632499	616.374802	547.624989	511.933028
440	440	455.273931	445.187393	540.719410	533.878747	494.162038	463.903751
450	450	412.634716	407.782064	486.338887	470.668103	439.022952	423.058343
460	460	373.835456	374.385834	435.779413	423.769869	395.053577	383.817218
470	470	345.071932	341.756972	394.146390	381.593027	361.412528	351.260451

5 rows × 301 columns

```
In [28]: # Calculate LogS for each measurement, rename wavelength column to Logwavelength, p
#https://www.geeksforgeeks.org/how-to-rename-columns-in-pandas-dataframe/
LogS=np.log10(Sstrans)
LogS.rename(columns = {'wavelength':'Logwavelength'}, inplace = True)
LogS.head()
LogS.to_csv("LogS.csv")
```

C:\Users\RobynHill\anaconda3\lib\site-packages\pandas\core\internals\blocks.py:40
2: RuntimeWarning: invalid value encountered in log10
result = func(self.values, **kwargs)

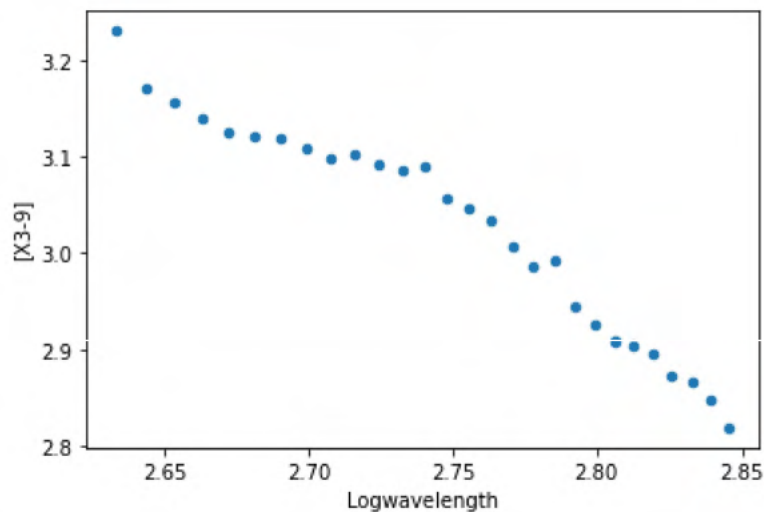
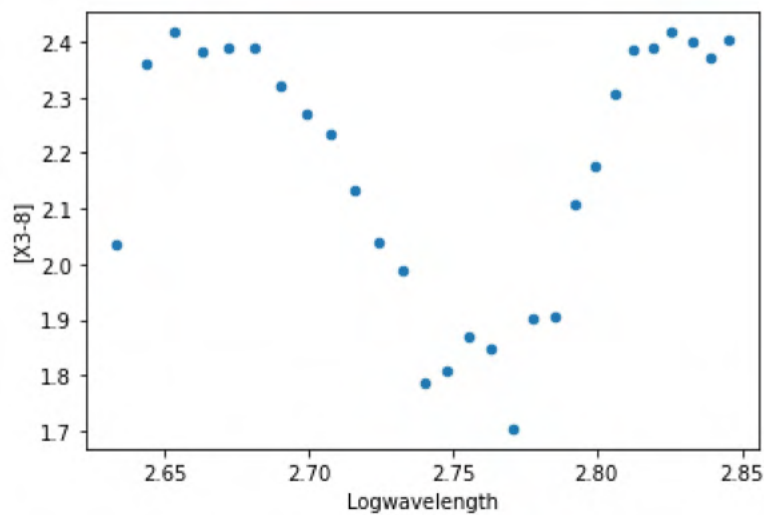
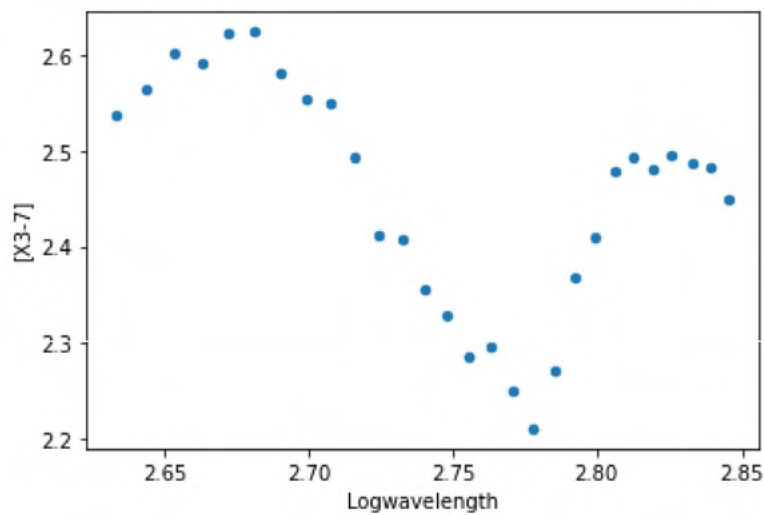
Out[28]:

	Logwavelength	U1-1	U1-2	U1-3	U1-4	U1-5	U1-6	U1-7
wavelength								
430	2.633468	2.752870	2.490898	3.119822	3.171085	2.985797	2.705649	2.516402
440	2.643453	2.793481	2.524718	3.054756	3.127225	2.989281	2.684340	2.540312
450	2.653213	2.783012	2.544153	3.044787	3.086824	2.943142	2.686273	2.533110
460	2.662758	2.759548	2.572208	3.019973	3.071791	2.917391	2.658773	2.545799
470	2.672098	2.783337	2.541049	2.997550	3.041277	2.912525	2.640646	2.520743

5 rows × 301 columns

```
In [43]: # Create plots of LogS as a function of Logwavelength for each measurement
#https://stackoverflow.com/questions/19189488/use-a-loop-to-plot-n-charts-python
#https://stackoverflow.com/questions/48569684/save-pandas-plots-created-in-a-loop-i
#https://stackoverflow.com/questions/24089264/saving-figures-in-a-loop
import matplotlib.pyplot as plt
for column in LogS.iloc[:,1:301]:
    LogS.plot(x='Logwavelength', y=[column], kind='scatter')
    plt.savefig(LogS[column].name + '.png')
```

C:\Users\RobynHill\anaconda3\lib\site-packages\pandas\plotting_matplotlib\core.p
y:386: RuntimeWarning: More than 20 figures have been opened. Figures created thro
ugh the pyplot interface (`matplotlib.pyplot.figure`) are retained until explicitl
y closed and may consume too much memory. (To control this warning, see the rcPara
m `figure.max\_open\_warning`).
fig = self.plt.figure(figsize=self.figsize)



```
In [31]: # Re-add warnings to allow code to be re-started from this point using the LogS csv
#https://www.packetswitch.co.uk/python-working-with-csv-files/
import warnings
warnings.simplefilter('ignore', FutureWarning)

import matplotlib
%matplotlib inline
import csv
from pandas import *
import pandas as pd
import numpy as np
LogS = read_csv('LogS.csv')
LogS.index = LogS['wavelength']
LogS.head()
```

Out[31]:

	wavelength	Logwavelength	U1-1	U1-2	U1-3	U1-4	U1-5	U1-	
	wavelength								
	430	430	2.633468	2.752870	2.490898	3.119822	3.171085	2.985797	2.70564
	440	440	2.643453	2.793481	2.524718	3.054756	3.127225	2.989281	2.68434
	450	450	2.653213	2.783012	2.544153	3.044787	3.086824	2.943142	2.68627
	460	460	2.662758	2.759548	2.572208	3.019973	3.071791	2.917391	2.65877
	470	470	2.672098	2.783337	2.541049	2.997550	3.041277	2.912525	2.64064

5 rows × 302 columns

```
In [32]: # Next step is to calculate gradient of LogS as a function of Logwavelength for each column
#https://www.w3schools.com/datascience/ds_linear_slope.asp
#https://www.askpython.com/python/coefficient-of-determination
#https://stackoverflow.com/questions/28647172/numpy-polyfit-doesnt-handle-nan-values
#https://stackoverflow.com/questions/16854200/how-to-skip-an-empty-column-with-pyth
for column in LogS.iloc[:,1:302]:
    x = LogS["Logwavelength"]
    y = LogS[column]
    idx = np.isfinite(x) & np.isfinite(y)
    try:
        LogS[column].name, np.polyfit(x[idx],y[idx],1)
        with open('Allwavelengthexponents2.csv', 'a') as a_file:
            writer_append = csv.writer(a_file)
            writer_append.writerow([LogS[column].name, np.polyfit(x[idx],y[idx],1)])
        writer_append.close()
    except:
        continue
```

```
In [33]: # Calculate R squared for each measurement of LogS as a function of Logwavelength
for column in LogS.iloc[:,1:302]:
    with open('Rsquareds.csv', 'a') as a_file:
        writer_append = csv.writer(a_file)
        writer_append.writerow([LogS[column].name, (np.corrcoef(LogS["Logwavelength"], LogS[column])[0,1])**2)]
    # writer_append.close()
```

```
In [35]: # Read in csv file of wavelength exponents as new data frame. Tidy up data by removing characters
#https://www.statology.org/pandas-remove-characters-from-string/
results=pd.DataFrame()
results = read_csv('Allwavelengthexponents2.csv')
results["Gradient"] = results["Gradient"].str.replace('[', '')
results["Gradient"] = results["Gradient"].str.replace(']', '')
results["Intercept"] = results["Intercept"].str.replace('[', '')
results["Intercept"] = results["Intercept"].str.replace(']', '')
results=results.dropna()
results.head()
```

```
Out[35]:
```

	Set	Gradient	Intercept
0	U1-1	-0.87255809	5.09638271
2	U1-2	-0.9638498	5.10428535
4	U1-3	-2.87278609	10.72481401
6	U1-4	-3.43086507	12.24961632
8	U1-5	-3.05167063	11.09163778

```
In [36]: # Repeat process for Rsquared values
Rsquareds = read_csv('Rsquareds.csv')
Rsquareds["Rsquared"] = Rsquareds["Rsquared"].str.replace(' ', '')
Rsquareds=Rsquareds.dropna()
Rsquareds.head()
```

```
Out[36]:
```

	Set	Rsquared
0	U1-1	0.92781671
2	U1-2	0.72636494
4	U1-3	0.86064203
6	U1-4	0.9401217
8	U1-5	0.91253584

```
In [37]: # Join waveLength exponents and Rsquared data sets together, print to check and exp
results=results.join(Rsquareds["Rsquared"])
results.head()
#results.to_csv("results.csv")
```

```
Out[37]:
```

	Set	Gradient	Intercept	Rsquared
0	U1-1	-0.87255809	5.09638271	0.92781671
2	U1-2	-0.9638498	5.10428535	0.72636494
4	U1-3	-2.87278609	10.72481401	0.86064203
6	U1-4	-3.43086507	12.24961632	0.9401217
8	U1-5	-3.05167063	11.09163778	0.91253584

```
In [ ]:
```

This code was written to calculate the wavelength exponent of MFC films. Ro refers to the measurement of the reflectivity of one MFC film over a black background. Roo refers to the measurement of the reflectivity of one MFC film over a stack copy paper. The reference Ro and Roo refer to one sheet of copy paper over a black background and a stack of copy paper over a black background.

The Kubelka-Munk approximation is used to calculate the S and K of the MFC film from this data, followed by creating plots of LogS vs Logwavelength which were used to calculate a wavelength exponent for the MFC film (ref G. Kortum, Reflectance Spectroscopy, Springer-Verlag, Germany, 1969)

The steps that are needed for this analysis to work are:

. Read both the Ro (MFC film) and Roo (MFC film over a stack of copy paper) measurements into Python and index by the wavelength . Read reference (copy paper) Ro and Roo into Python and index by the wavelength . Read in the equations needed to calculate S and K for the MFC film using the Kubelka-Munk approximation . Calculate LogS for each measurement for each wavelength . Plot LogS against Logwavelength for each measurement . Calculate the slope and Rsquared of LogS as a function of Logwavelength for each measurement and output to csv . Calculate average slope and Rsquared for each MFC sample . This code was developed by editing the Python script to calculate light scattering of MFC coatings

```
In [4]: import warnings
warnings.simplefilter('ignore', FutureWarning)

import matplotlib
#matplotlib.rcParams['axes.grid'] = True
%matplotlib inline
import csv
from pandas import *
import pandas as pd
```

```
In [5]: #https://stackoverflow.com/questions/1810743/how-to-set-the-current-working-directo
import os
os.getcwd()
os.chdir("C:\\Users\\RobynHill\\OneDrive - FiberLean Technologies\\Big Pulp\\Light
```

```
In [6]: #First step is to read in csv files for Ro and Roo and check that the data is displ
Romeasured = read_csv('Romeasured.csv')
Romeasured.head()
Romeasured.index = Romeasured['wavelength']
Romeasured.head(2)
```

```
Out[6]:
```

	wavelength	FILM A3	A3-2	A3-3	A3-4	A3-5	A3-6	A3-7	A3-8	A3-9	...	
	430	430	41.507	41.421	41.489	41.378	41.513	41.816	41.617	40.232	40.402	...
	440	440	41.679	41.614	41.648	41.545	41.666	42.000	41.820	40.391	40.601	...

2 rows × 71 columns

```
In [7]: Roomeasured = read_csv('Roomeasured.csv')
Roomeasured.head()
Roomeasured.index = Roomeasured['wavelength']
Roomeasured.head(2)
```

```
Out[7]:
```

	wavelength	FILM A3	A3-2	A3-3	A3-4	A3-5	A3-6	A3-7	A3-8	A3-9	...
	wavelength										
	430	430	74.818	74.906	75.535	75.400	75.476	75.525	75.553	75.259	75.235 ...
	440	440	77.402	77.440	77.905	77.978	77.923	78.011	77.995	77.750	77.697 ...

2 rows × 71 columns

```
In [12]: #Need average Ro and Roo for each wavelength for the reference values (copy paper).
#Input Ro and Roo averages as separate csv file.
```

```
Reference_mean = read_csv('Reference_mean_data.csv')
Reference_mean.head()
Reference_mean.index = Reference_mean['wavelength']
Reference_mean.head(2)
```

```
Out[12]:
```

	wavelength	Mean Ro	Reference	Mean Roo	reference
	wavelength				
	430	430	79.647	87.362	
	440	440	80.117	88.768	

```
In [13]: # Divide Ro reference and Roo reference by 100 to be used in calculations.
# Add a parameter for Log10wavelength
#https://pythonforundergradengineers.com/exponents-and-logs-with-python.html
import numpy as np
def divideby100 (value):
    return (value/100)
RRO = 'Mean Ro Reference'
Reference_mean[RRO] = Reference_mean[RRO].apply(divideby100)
RROO = 'Mean Roo reference'
Reference_mean[RROO] = Reference_mean[RROO].apply(divideby100)
WAVELENGTH = 'wavelength'

Reference_mean.head()
```

```
Out[13]:
```

	wavelength	Mean Ro	Reference	Mean Roo	reference
	wavelength				
	430	430	0.79647	0.87362	
	440	440	0.80117	0.88768	
	450	450	0.80117	0.89354	
	460	460	0.80118	0.89693	
	470	470	0.80047	0.89807	

```
In [14]: # Next step is to read in the gsm of the films and index by wavelength
GSM = read_csv('GSM.csv')
GSM
GSM.index = GSM['wavelength']
GSM.head()
```

```
Out[14]:
```

	wavelength	FILM A3	A3-2	A3-3	A3-4	A3-5	A3-6	A3-7	A3-8	A3-9	...	FILM E6	E
	wavelength												
	430.0	430.0	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	...	47.1	47
	440.0	440.0	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	...	47.1	47
	450.0	450.0	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	...	47.1	47
	460.0	460.0	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	...	47.1	47
	470.0	470.0	49.58	49.58	49.58	49.58	49.58	49.58	49.58	49.58	...	47.1	47

5 rows × 71 columns

```
In [17]: # Kubelka-Munk approximation calulcations for S and K
# R1 is the measured reflectance of an MFC film over a black background
# R2 is the measured reflectance of an MFC film over a stack of copy paper
# Rooreal is the true value of Roo for the MFC films
# S is the scattering coefficient given in cm^2/g, K is the absorption coefficient
# https://www.datasciencemadesimple.com/Log-natural-Logarithmic-value-column-pandas

def a(R1,Ro,RROO):
    a = 0.5*((R1/100)+(((Ro/100)-(R1/100)+RROO)/((Ro/100)*RROO)))
    return a

def b(a):
    b = ((a**2)-1)**0.5
    return b

def Roo(a,b):
    Rooreal = a-b
    return Rooreal

import numpy as np
def S(GSM,b,Ro,Rooreal):
    S = (1/((GSM/10000)*2*b))*(np.log((1-(Ro/100)*Rooreal)/(1-(Ro/100)/Rooreal)))
    return S

def K(S,Rooreal):
    K = S*(((1-Rooreal)**2)/(2*Rooreal))
    return (K)
```

```
In [18]: #Create data frame for A calculations
#https://www.tutorialspoint.com/how-to-create-a-dataframe-in-python
As=pd.DataFrame()
```

```
In [19]: #Calculate As
#https://sparkbyexamples.com/pandas/pandas-iterate-over-columns-of-dataframe-to-run
#https://www.projectpro.io/recipes/append-output-of-for-loop-python-dataframe#:~:te
#https://stackoverflow.com/questions/62931809/cannot-concatenate-object-of-type-cla
#https://sparkbyexamples.com/pandas/pandas-iterate-over-columns-of-dataframe-to-run
```

```
# https://www.geeksforgeeks.org/different-ways-to-iterate-over-rows-in-pandas-dataframe/
# https://sparkbyexamples.com/pandas/iterate-over-rows-in-pandas-dataframe/#:~:text=Use%20the%20T%20attribute%20to%20iterate%20over%20all%20columns%20of%20a%20dataframe,~:text=Use%20the%20T%20attribute%20to%20iterate%20over%20all%20columns%20of%20a%20dataframe
for column in Romeasured.iloc[:71]:
    for column in Romeasured.iloc[:71]:
        As=As.append(a(Romeasured[column], Romeasured[column], Reference_mean[RROO
    break
break
```

```
Input In [19]
break
^
SyntaxError: 'break' outside loop
```

```
In [20]: #https://stackoverflow.com/questions/36846060/how-to-replace-an-entire-column-on-pandas-dataframe
#https://note.nkmk.me/en/python-pandas-t-transpose/#:~:text=Use%20the%20T%20attribute%20to%20iterate%20over%20all%20columns%20of%20a%20dataframe
Astrans=As.T
Astrans.columns=Romeasured.columns
Astrans["wavelength"]=Romeasured["wavelength"]
Astrans.head()
Astrans.to_csv("Astrans.csv")
```

```
Out[20]:
```

	wavelength	FILM A3	A3-2	A3-3	A3-4	A3-5	A3-6	A3-7
wavelength								
430	430	1.119388	1.118971	1.113157	1.114787	1.113581	1.111968	1.112498
440	440	1.103881	1.103796	1.099707	1.099447	1.099490	1.097584	1.098341
450	450	1.091861	1.092362	1.088716	1.088706	1.087895	1.087095	1.087262
460	460	1.082414	1.083427	1.079505	1.079830	1.079024	1.078166	1.078800
470	470	1.074674	1.075681	1.072842	1.072846	1.072083	1.070945	1.071763

5 rows × 71 columns

```
In [21]: #Calculate Bs
Bs=pd.DataFrame()
for column in Astrans.iloc[:71]:
    Bs=Bs.append(b(Astrans[column]),ignore_index=True)#,index=Reference_mean["wavelength"]
break
```

```
Input In [21]
break
^
SyntaxError: 'break' outside loop
```

```
In [22]: Bstrans=Bs.T
Bstrans.columns=Astrans.columns
Bstrans["wavelength"]=Romeasured["wavelength"]
Bstrans.head()
```

```
Out[22]:
```

	wavelength	FILM A3	A3-2	A3-3	A3-4	A3-5	A3-6	A3-7
	wavelength							
430	430	0.503020	0.502092	0.488997	0.492697	0.489962	0.486285	0.487495
440	440	0.467496	0.467296	0.457554	0.456928	0.457033	0.452428	0.454260
450	450	0.438361	0.439607	0.430467	0.430442	0.428387	0.426350	0.426778
460	460	0.414272	0.416910	0.406610	0.407470	0.405332	0.403040	0.404733
470	470	0.393605	0.396346	0.388575	0.388586	0.386472	0.383305	0.385584

5 rows × 71 columns

```
In [23]: Rooreals=Astrans=Bstrans
Rooreals["wavelength"]=Romeasured["wavelength"]
Rooreals.head()
#Rooreals.to_csv("Rooreals.csv")
```

```
Out[23]:
```

	wavelength	FILM A3	A3-2	A3-3	A3-4	A3-5	A3-6	A3-7
	wavelength							
430	430	0.616368	0.616879	0.624160	0.622090	0.623619	0.625683	0.625003
440	440	0.636385	0.636500	0.642153	0.642519	0.642458	0.645156	0.644081
450	450	0.653500	0.652755	0.658249	0.658264	0.659508	0.660744	0.660485
460	460	0.668143	0.666517	0.672895	0.672359	0.673693	0.675126	0.674067
470	470	0.681069	0.679335	0.684267	0.684260	0.685610	0.687640	0.686179

5 rows × 71 columns

```
In [24]: #https://www.prepbytes.com/blog/python/iloc-function-in-python/#:~:text=The%20iloc%
Ss=pd.DataFrame()
for column in GSM.iloc[:71]:
    for column in Bstrans.iloc[:71]:
        for column in Romeasured.iloc[:71]:
            for column in Rooreals.iloc[:71]:
                Ss=Ss.append(S(GSM[column],Bstrans[column], Romeasured[column], Rooreals[column]))
            break
        break
    break
break
```

C:\Users\RobynHill\anaconda3\lib\site-packages\pandas\core\arraylike.py:397: RuntimeWarning: invalid value encountered in log
result = getattr(ufunc, method)(*inputs, **kwargs)

Input In [24]

break

SyntaxError: 'break' outside loop

```
In [25]: Sstrans=Ss.T
Sstrans.columns=Astrans.columns
Sstrans["wavelength"]=Astrans["wavelength"]
```

```
Sstrans.head()
#Sstrans.to_csv("Sstrans.csv")
```

```
Out[25]:
```

	wavelength	FILM A3	A3-2	A3-3	A3-4	A3-5	A3-6
	wavelength						
430.0	430	165.110983	164.304936	163.559919	163.019974	163.849430	165.964938
440.0	440	163.041520	162.507017	161.892630	161.032716	161.987145	164.203822
450.0	450	160.794533	159.927313	159.934030	158.881732	159.855616	162.172208
460.0	460	158.655675	157.915806	157.821918	157.261583	158.086906	160.247557
470.0	470	156.877951	156.363565	155.773292	155.365450	156.396102	158.489177

5 rows × 71 columns

```
In [26]: Ks=pd.DataFrame()
for column in Sstrans.iloc[:71]:
    for column in Rooreals.iloc[:71]:
        Ks=Ks.append(K(Sstrans[column], Rooreals[column]),ignore_index=True)#, index=column)
    break
break
```

```
Input In [26]
break
^
SyntaxError: 'break' outside loop
```

```
In [27]: Kstrans=Ks.T
Kstrans.columns=Astrans.columns
Kstrans["wavelength"]=Romeasured["wavelength"]
Kstrans.head()
#Kstrans.to_csv("Kstrans.csv")
```

```
Out[27]:
```

	wavelength	FILM A3	A3-2	A3-3	A3-4	A3-5	A3-6	A3-7
	wavelength							
430.0	430	19.712233	19.547516	18.507944	18.712561	18.610193	18.582762	18.5007
440.0	440	16.936841	16.867597	16.141841	16.014154	16.116145	16.023699	16.0244
450.0	450	14.770725	14.771161	14.188632	14.093759	14.050504	14.124312	14.0299
460.0	460	13.075517	13.174435	12.547701	12.554147	12.492732	12.525835	12.5497
470.0	470	11.714781	11.833780	11.346889	11.317785	11.273429	11.243965	11.2945

5 rows × 71 columns

```
In [30]: #https://www.geeksforgeeks.org/how-to-rename-columns-in-pandas-dataframe/
LogS=np.log10(Sstrans)
LogS.rename(columns = {'wavelength':'Logwavelength'}, inplace = True)
LogS.head()
```

Out[30]:

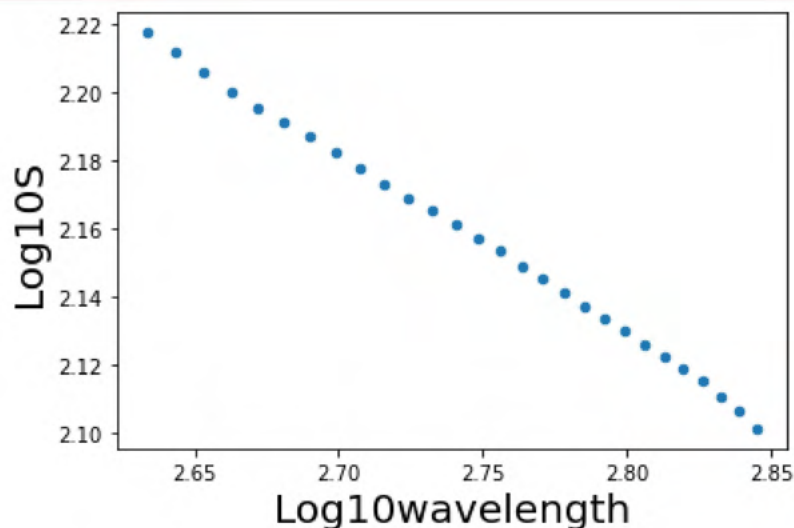
	Logwavelength	FILM A3	A3-2	A3-3	A3-4	A3-5	A3-6	A3-7
wavelength								
430.0	2.633468	2.217776	2.215651	2.213677	2.212241	2.214445	2.220016	2.216045
440.0	2.643453	2.212298	2.210872	2.209227	2.206914	2.209481	2.215383	2.212049
450.0	2.653213	2.206271	2.203923	2.203941	2.201074	2.203728	2.209976	2.206229
460.0	2.662758	2.200456	2.198426	2.198167	2.196623	2.198896	2.204791	2.202090
470.0	2.672098	2.195562	2.194136	2.192493	2.191354	2.194226	2.200000	2.196971

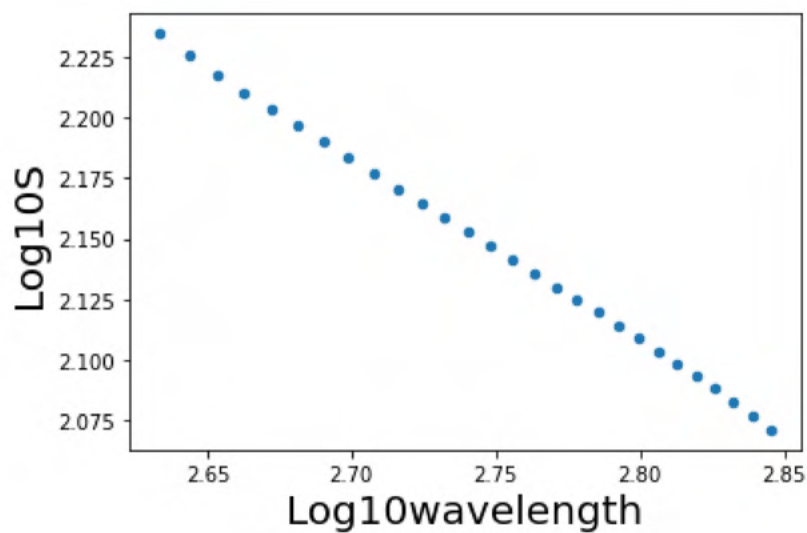
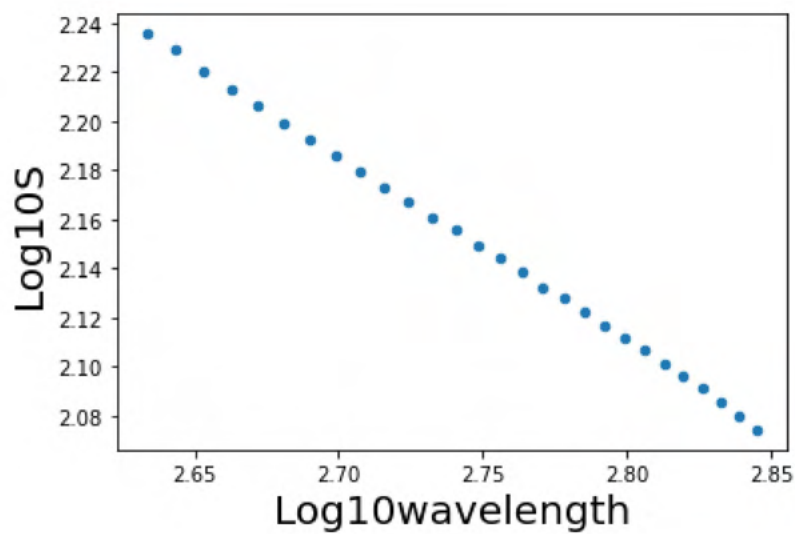
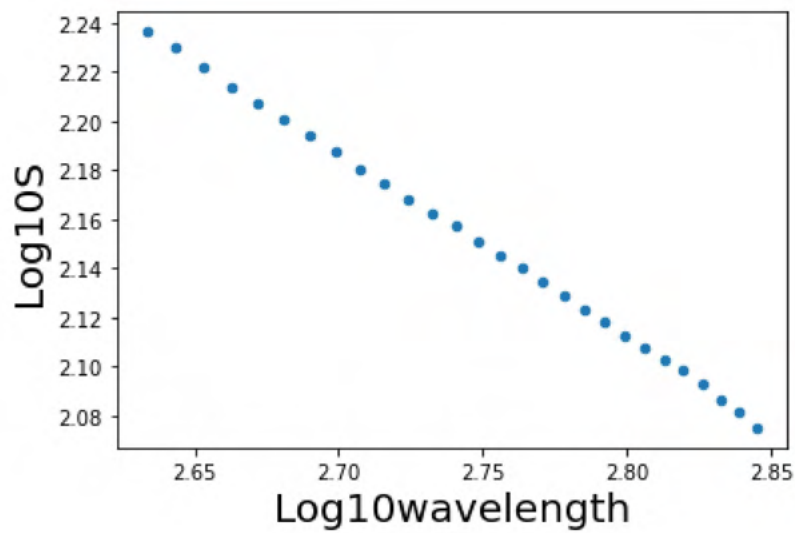
5 rows × 71 columns

```
In [31]: #https://stackoverflow.com/questions/19189488/use-a-loop-to-plot-n-charts-python
#https://stackoverflow.com/questions/48569684/save-pandas-plots-created-in-a-loop-i
#https://stackoverflow.com/questions/24089264/saving-figures-in-a-loop
#https://www.scaler.com/topics/matplotlib/matplotlib-axis-label/
import matplotlib.pyplot as plt
for column in LogS.iloc[:,1:71]:
    LogS.plot(x='Logwavelength', y=[column], kind='scatter')
    plt.xlabel('Log10wavelength', fontsize=20)
    plt.ylabel('Log10S', fontsize=20)
    plt.savefig(LogS[column].name + '.png')
```

C:\Users\RobynHill\anaconda3\lib\site-packages\pandas\plotting_matplotlib\core.py:386: RuntimeWarning: More than 20 figures have been opened. Figures created through the pyplot interface (`matplotlib.pyplot.figure`) are retained until explicitly closed and may consume too much memory. (To control this warning, see the rcParam `figure.max\_open\_warning`).

```
fig = self.plt.figure(figsize=self.figsize)
```





```
In [32]: import warnings
warnings.simplefilter('ignore', FutureWarning)

import matplotlib
#matplotlib.rcParams['axes.grid'] = True
%matplotlib inline
import csv
from pandas import *
import pandas as pd
import numpy as np
LogS = read_csv('LogS.csv')
```

```
In [33]: LogS.index = LogS['wavelength']
LogS.head()
```

```
Out[33]:
```

	wavelength	Logwavelength	FILM A3	A3-2	A3-3	A3-4	A3-5	A3-6
	430.0	430.0	2.633468	2.217776	2.215651	2.213677	2.212241	2.214445
	440.0	440.0	2.643453	2.212298	2.210872	2.209227	2.206914	2.209481
	450.0	450.0	2.653213	2.206271	2.203923	2.203941	2.201074	2.203728
	460.0	460.0	2.662758	2.200456	2.198426	2.198167	2.196623	2.198896
	470.0	470.0	2.672098	2.195562	2.194136	2.192493	2.191354	2.194226

5 rows × 9 columns

```
In [34]: results=pd.DataFrame()
results
```

```
Out[34]:
```

```
In [35]: #https://www.w3schools.com/datascience/ds_linear_slope.asp
#https://www.askpython.com/python/coefficient-of-determination
#https://stackoverflow.com/questions/28647172/numpy-polyfit-doesnt-handle-nan-values
#https://stackoverflow.com/questions/16854200/how-to-skip-an-empty-column-with-pyth
for column in LogS.iloc[:,1:98]:
    x = LogS["Logwavelength"]
    y = LogS[column]
    idx = np.isfinite(x) & np.isfinite(y)
    try:
        LogS[column].name, np.polyfit(x[idx],y[idx],1)
        with open('Allwavelengthexponents2.csv', 'a') as a_file:
            writer_append = csv.writer(a_file)
            writer_append.writerow([LogS[column].name, np.polyfit(x[idx],y[idx],1)])
            writer_append.close()
    except:
        continue
```

```
In [36]: for column in LogS.iloc[:,1:98]:
    with open('Rsquareds.csv', 'a') as a_file:
        writer_append = csv.writer(a_file)
        writer_append.writerow([LogS[column].name,(np.corrcoef(LogS["Logwavelength"],
# writer_append.close()
```

```
In [37]: results = read_csv('Allwavelengthexponents2.csv')
results.head()
```

Out[37]:

	Set	gradient	intercept
0	FILM A3	[-0.53243773	3.619553
1	NaN	NaN	NaN
2	A3-2	[-0.53399178	3.62169792]
3	NaN	NaN	NaN
4	A3-3	[-0.54028388	3.63732853]

In [38]: [#https://www.statology.org/pandas-remove-characters-from-string/](https://www.statology.org/pandas-remove-characters-from-string/)

```

results["gradient"] = results["gradient"].str.replace('[', '')
results["gradient"] = results["gradient"].str.replace(']', '')
results["intercept"] = results["intercept"].str.replace('[', '')
results["intercept"] = results["intercept"].str.replace(']', '')
results=results.dropna()
results.head()

```

Out[38]:

	Set	gradient	intercept
0	FILM A3	-0.53243773	3.619553
2	A3-2	-0.53399178	3.62169792
4	A3-3	-0.54028388	3.63732853
6	A3-4	-0.53624181	3.6249178
8	A3-5	-0.5260085	3.60061828

In [39]:

```

Rsquareds = read_csv('Rsquareds.csv')
Rsquareds.head()

```

Out[39]:

	Set	Rsquared
0	FILM A3	0.99909274]
1	NaN	NaN
2	A3-2	0.99915507]
3	NaN	NaN
4	A3-3	0.999213]

In [41]:

```

Rsquareds["Rsquared"] = Rsquareds["Rsquared"].str.replace(']', '')
Rsquareds=Rsquareds.dropna()
Rsquareds.head()

```

Out[41]:

	Set	Rsquared
0	FILM A3	0.99909274
2	A3-2	0.99915507
4	A3-3	0.999213
6	A3-4	0.9992836
8	A3-5	0.99891888

```
In [42]: results=results.join(Rsquareds["Rsquared"])
results.head()
```

```
Out[42]:
```

	Set	gradient	intercept	Rsquared
0	FILM A3	-0.53243773	3.619553	0.99909274
2	A3-2	-0.53399178	3.62169792	0.99915507
4	A3-3	-0.54028388	3.63732853	0.999213
6	A3-4	-0.53624181	3.6249178	0.9992836
8	A3-5	-0.5260085	3.60061828	0.99891888

```
In [62]: results.to_csv("results.csv")
```

```
In [ ]:
```