

# **THE EFFECT OF MICROFIBRILLATED CELLULOSE ON THE STRENGTH AND LIGHT SCATTERING OF HIGHLY FILLED PAPERS**

*J.Phipps, T.Larson, D.Ingle, H.Eaton,*

FiberLean Technologies Ltd., Par Moor Centre, Cornwall, PL24 2SQ, UK

## **ABSTRACT**

There has been much recent interest in the use of microfibrillated and nanofibrillated cellulose as additives to improve the mechanical properties of paper. Most of the original methods used to make these materials are too costly for this purpose, but now purely mechanical processes are becoming available which have made it a more practical possibility. The tensile strength of unfilled paper and its relation to light scattering have been the subject of extensive theoretical and experimental research, and the effects of addition of fibrillated cellulose have been considered by several authors in the light of this work. However, much less theoretical work has been dedicated to the properties of papers with high filler contents.

In the FiberLean process, fibres are mixed with filler and ground together until the fibres are converted into microfibrillated cellulose, a few per cent of which can be added to paper to increase its strength and allow a substantially higher filler content. We build on the work of Bown to develop a model for the effect of filler on paper tensile strength and light scattering, and use this to investigate the mechanism by which mfc improves these in highly filled paper. We further demonstrate some of the advantages of its use over the conventional refining approach. These include process flexibility and some specific paper properties such as increased elasticity and higher resistance to tearing.

## **INTRODUCTION**

Uncoated paper is made from two major components – pulp fibres and mineral fillers. The pulp fibres provide the structure and strength of the paper, whilst the mineral fillers provide optical and printing properties. Fibres in paper form a network, which gains its strength from bonds between fibres at their contact points. The amount of filler that can be incorporated into paper is limited by its effect on network strength, because filler particles reduce the total area of intimate contact between fibres.

Many theories have been proposed over the years to explain and model the tensile strength of an unfilled paper sheet. All of these models consider paper as a network of fibres with a distribution

of orientations. Cox [1] proposed the first model for paper modulus and strength, in which he considered a network of long, straight fibres of random orientation which carry their load only at their ends, which are situated at the edges of the paper sheet and strongly bonded together. Page and Seth [2] later modified this model for modulus taking into account stress transfer between fibres strongly bonded together, and verified it experimentally. Kallmes [3] calculated the whole stress vs. elongation curve using similar assumptions to Cox, but including bonds between fibres which can fail during straining of the sheet. Page [4] introduced the most widely cited model, which also takes interfibre bonding into account; it considers a failure zone in which the load is successively transferred onto fewer and fewer fibres as bonds between them are successively broken. Failure of the sheet occurs when the remaining load-bearing fibres become overloaded and either break or are pulled out of the network. Karenlampi [5] modified the Kallmes approach to include mixtures of fibres of different properties. More recently, Carlsson and Lindstrom [6] proposed a modified shear-lag model and used it to investigate the effects of fibre length on the transition between fibre pull-out and fibre breakage.

The Page model (equation 1) conveniently consists of two terms, the first of which represents fibre breakage and the second of which represents bond failure

$$\frac{1}{T} = \frac{9}{8Z} + \frac{12A\rho_w}{bPL(RBA)} \quad (1)$$

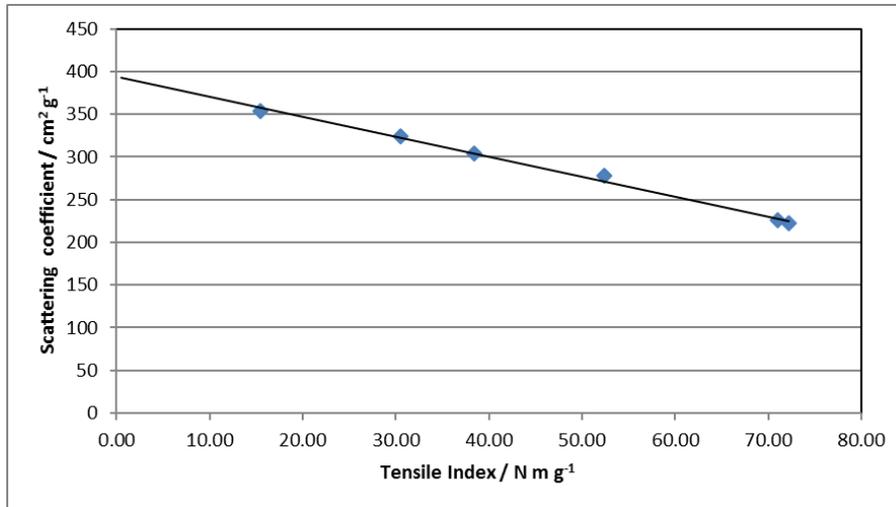
$T$  is the paper tensile strength index ( $\text{Nm g}^{-1}$ ),  $Z$  is the zero-span tensile index ( $\text{Nm g}^{-1}$ ),  $A$  is the average fibre cross sectional area ( $\text{m}^2$ ),  $P$  is the perimeter of the fibre cross-section (m),  $L$  is the fibre length (m),  $\rho_w$  is the fibre density ( $\text{kg m}^{-3}$ ),  $b$  is the shear bond strength per unit area (Pa), and  $RBA$  is the ‘relative bonded area’, i.e. the fraction of fibre surface area that is bonded to others.

For most graphic papers, the fibres are sufficiently strong that the first term of this equation is small compared with the second, and tensile failure occurs principally by the breaking of bonds. Papermakers can increase strength by refining the fibres, which increases their flexibility and separates some of the fibrils which make up the fibres at the fibre surface, thus increasing the bonded area once the fibres are made into a sheet. To a first approximation, refining does not significantly affect the other fibre properties that go into the Page equation.

## THE RELATIONSHIP BETWEEN LIGHT SCATTERING, STRENGTH AND BONDED AREA IN UNFILLED PAPERS

In order to use the various models to calculate paper strength, a measurement or estimate of the relative bonded area is required. Light scattering from unfilled paper sheets occurs at the unbonded surfaces of the fibres, and can be used to estimate the area of bonded surface. Ingmanson and Thode [7] proposed a simple method, whereby sheets are made from fibres from the same source, but refined to different degrees, and the light scattering coefficient,  $S$  ( $\text{cm}^2 \text{g}^{-1}$ ), of the sheets is plotted against their tensile strength. Extrapolation to zero strength gives the scattering from the totally unbonded fibres,  $S_0$ . Assuming that the scattering is linearly proportional to the unbonded area, the relative amount of bonded area,  $A$ , of the sheets is then given by  $A = 1 - S/S_0$ .

The extrapolation to zero strength for  $S_0$  is often considered a significant limitation of this method [8]. The main problem is that a sheet made from unrefined fibres may still have significant strength, so that all points lie far from the zero-strength intercept and the extrapolation amplifies any measurement errors. Some authors have made unrefined sheets without pressing or dried them from non-aqueous solvents to reduce the bonded area to alleviate this. Batchelor and He [9,10] proposed an alternative method, in which the sheet density and fibre cross-sectional shape are used to calculate the RBA instead. This method has the advantage that it can be used in the analysis of machine-made papers where it is not possible to make comparable sheets from unrefined fibres, but it requires a detailed analysis of fibre dimensions by microscopy. The use of the RBA determined by the Ingmanson and Thode method in the Page equation also assumes that basic fibre dimensions do not change on refining. Any reduction in fibre length not only changes another parameter in the Page equation, but also if sheets with substantially different fibre lengths are used in the extrapolation, the assumption that the variation in strength depends only on the variation in RBA is incorrect. Batchelor and He [11] showed that introduction of short fibres into a furnish causes an increase in scattering but a decrease in strength, thus reducing the value of  $S_0$  by extrapolation when clearly it should be increased. However, for moderate refining, modern image analysis instruments show that basic fibre dimensions do not change significantly. Thus for a handsheet study in which unrefined and unpressed sheets can be included and the pulp furnish used is constant, it can be still be used to give a reasonable estimation of the RBA. Figure 1 is an example of this from our laboratory – here a bleached pine Kraft pulp has been refined in a Valley beater to different degrees and made into unfilled handsheets whose tensile index and scattering coefficient have been measured by standard methods.



**Figure 1.** Determination of  $S_0$  and bonded area. Bleached softwood Kraft pulp refined at different times in a Valley Beater

## THE EFFECT OF MINERAL FILLERS ON SHEET STRENGTH AND LIGHT SCATTERING

The majority of theoretical models of paper strength consider only unfilled sheets, whereas most commercial graphic papers contain mineral fillers. The presence of fillers in paper leads to several effects, which are discussed in a recent comprehensive review by Hubbe and Gill [12]. Filler particles deposit on the fibre surfaces and reduce the bonded contact area between them, and they contribute strongly to light scattering. Reduction in bonding is inferred from the loss of strength, as well as the fact that the density of filled sheets is generally reduced when the mass of the filler is subtracted. In experiments by Bown [13], sheets were filled with calcium carbonate fillers which were then dissolved in a solution of acid in ethanol, in order to preserve the structure of the sheet after drying. The dissolution process did not affect the absolute strength of the sheets, and their light scattering coefficients were significantly higher than that of the corresponding unfilled sheet. According to the Ingmanson and Thode extrapolation this would imply reduced bonding and thus higher scattering from the fibres compared with the unfilled sheet. Alinec and Lepoutre [14] compared unfilled sheets and sheets filled with  $\text{TiO}_2$  particles at the same strength in order to decouple scattering from the filler and the debonded fibres. Furthermore, Bown [13] also showed that fillers prevent fibrils that are located on free fibre surfaces away from contact areas from collapsing onto the fibre surfaces during drying, which generates further light scattering which would not be accounted for in the Ingmanson and Thode model. He also demonstrated that whilst, in unfilled sheets, increasing refining leads to an increase in bonded area and a reduction in light scattering, in highly filled sheets, the extra contribution of the fibrils leads to an increase in light scattering with refining. Alinec [15] showed that, because typical fillers (with the exception of

TiO<sub>2</sub>) and fibres have approximately the same refractive index, paper can be considered as a porous solid, such that light is scattered from the internal pores, and the scattering coefficient is proportional to the total volume of pores larger than 200nm in diameter which scatter light efficiently. Although fine particle size fillers (median size 0.4 to 1 µm) are the most efficient at generating pores of the correct dimensions, they are also more detrimental to sheet strength. Nevertheless, fine particle size fillers will typically generate more light scattering per unit strength lost than coarse ones [16,17]. However, since higher loading levels can be achieved with coarser fillers and they are easier to retain, typical filler grades have a median size of around 2 µm.

There appear to be very few publications describing quantitative theories of the effect of fillers on paper strength. Beazley [18,19] used the Page equation, and assumed that the addition of filler replaces fibre/fibre bonds with fibre/filler and filler/filler bonds. Because he expected the area of overlap between the fibres to be approximately the same in filled papers as in unfilled ones, he assumed that the RBA stays constant. Thus the shear bond strength  $b$  in equation 1 is replaced with an average bond strength which depends on the relative surface area of filler and fibre present, so that

$$b = \frac{b_m L S_m + b_f (1 - L) S_f}{L S_m + (1 - L) S_f} \quad (2)$$

Here  $b_m$  and  $b_f$  are the shear bond strengths of filler/filler and fibre/fibre bonds respectively,  $S_m$  and  $S_f$  are the specific surface areas (m<sup>2</sup> g<sup>-1</sup>) of filler and fibre available for bonding, and  $L$  is the mass fraction of filler. Modifying the Page equation in this way leads to a linear relationship of the form

$$\frac{T_L T}{(T - T_L)} = k \frac{(1 - L)}{L S_m} + c \quad (3)$$

where  $T$  and  $T_L$  are the tensile strengths of the unfilled and filled sheets,  $k$  and  $c$  are constants. Plots of this type for a variety of broad and narrow size fraction kaolin fillers and loadings were shown to be reasonably linear, at least at filler levels where the sheet strength is significantly reduced compared with the unfilled sheet, and to pass approximately through the origin; since  $c$  depends upon the strength of a filler/filler bond which was expected to be very weak, this was as expected.

Beazley's assumption that the bonded area remains constant and that fibre/fibre bonds are replaced by weaker filler/filler bonds is not generally accepted. Most authors agree that the presence of filler reduces the relative bonded area, and that the contribution of filler/filler bonds is negligible. Furthermore, whilst a good correlation between the specific surface area of fillers and their effect on sheet strength was observed for kaolin fractions of similar shape, it is not observed when different shapes and aggregated fillers such as precipitated calcium carbonates are considered together. Li and Pelton [20] investigated the effect of filler-induced debonding directly by depositing fillers on wet sheets that were then pressed together and dried, and measuring the

delamination peel force. They considered the fillers to be randomly distributed on the fibre surfaces, and that each filler particle leads to a fixed area of unbonded surface, which may overlap with that from other particles. This led to a prediction that the peel force should decrease exponentially with filler loading, which was observed experimentally. The data and model were also used to estimate the area debonded per filler particle, which was shown to be substantially higher than the projected area of the particle, assuming it to be spherical.

Bown [13] proposed a quantitative model for the calculation of the light scattering coefficient of filled sheets which is comprised of 3 components. Firstly, scattering occurs from the surfaces of unbonded fibres which are not disturbed by filler, and where any fibrils have been collapsed onto the fibres by the drying process. According to the relationship demonstrated in Figure 1, for the unfilled sheet the tensile strength is directly proportional to the bonded area. Addition of filler reduces the bonded area and the tensile strength in the same way, so that the ratio of the bonded area of the filled sheet to the unfilled,  $A_L/A$ , is equal to the ratio of the tensile strength per unit fibre mass of the filled sheet to the unfilled,  $T_L/T$ .

$$\frac{A_L}{A} = \frac{T_L}{T} \quad (4)$$

Thus the scattering from the unbonded, unfibrillated fibres is given by

$$\text{Fibre scattering} = (1 - L) \left(1 - \frac{T_L}{T}\right) S_0 \quad (5)$$

$S_0$  and  $T$  are as defined in the preceding section, and  $L$  is the mass fraction of the filler. For the contribution of the fibrils to the scattering, Bown denoted the fraction of fibre surface covered by filler (and thus prevented from bonding) as  $x$ , so that the fibre area not covered by filler is  $(1 - x)$ . The strength of the filled sheet per unit fibre mass is then proportional to the probability that uncovered surfaces come together to form a bond,  $(1 - x)^2$ . The relative strength of the filled sheet to the unfilled  $T_L/T$  is also  $(1 - x)^2$ , so that  $x = (1 - \sqrt{T_L/T})$ , because  $x$  is zero in the unfilled sheet. The scattering from the uncollapsed fibrils, which also occurs on the fraction of surface occupied by filler,  $x$ , is then given by

$$\text{Fibril scattering} = \left(1 - \sqrt{\frac{T_L}{T}}\right) (S_{fibrils} - S_0)(1 - L) \quad (6)$$

Here  $S_{fibrils}$  is the scattering coefficient ( $\text{cm}^2 \text{g}^{-1}$ ) from fibre surfaces covered with fibrils which are prevented from collapse by the filler. It was directly measured in two ways: either by dissolving calcium carbonate filler from sheets or by drying sheets from acetone to prevent the fibril collapse, and then comparing the scattering with similar, unfilled sheets. Finally, the scattering from the filler particles themselves is simply proportional to the mass fraction of filler and the filler scattering coefficient  $S_{filler}$  ( $\text{cm}^2 \text{g}^{-1}$ ):

$$\text{Filler scattering} = LS_{\text{filler}} \quad (7)$$

In a later publication [16], Bown discussed the relationship between the size and shape distribution of the filler and its effect on sheet strength. Whilst he did not define an explicit relationship between strength and filler content, he did suggest a relation between the debonding effect of the filler and the increase in fibre bulk that it causes, and showed that this depends on the size of the filler particles (or aggregates of particles in the case of aggregated fillers like PCC or calcined clay). The increase in sheet bulk *vs.* the loss in tensile strength (both expressed per unit fibre mass) was shown to be approximately linear and dependent upon the filler or aggregate particle size. The parameter  $t$  was defined, which is a fixed characteristic of the filler and represents the spacing of debonded areas of fibre caused by the filler. Values of  $t$  in  $\mu\text{m}$  for different fillers were determined from plots of the increase in fibre bulk as a function of strength loss. It was also shown that, for a range of narrow particle size distribution fillers, the filler content required to reduce sheet strength per unit fibre mass by 30% was approximately linear with  $t$ . Note that although fillers with larger values of  $t$  give larger spacing between the fibres than those with smaller  $t$ , and thus more debonding per particle, they contain fewer particles per unit mass, and require a higher loading to reduce strength by a given amount.

In this paper, we have applied Bown's analysis of the relationship between strength and light scattering in filled papers, both in the absence and presence of microfibrillated cellulose (mfc), in order to gain an understanding of the mechanism by which the mfc influences these properties. For this, it was necessary to define a relationship between filler content and tensile strength that is compatible with all of the above observations.

The ratio  $T_L/T$  is dependent on both the filler content,  $L$ , and the filler parameter,  $t$ . Firstly we note that the linear relationship between  $t$  and the filler content required to reduce strength by 30% implies that when  $T_L/T = 70\%$ ,  $L = \text{constant} \times t$  for all values of  $t$ . Secondly we consider the  $x$  parameter, which is the proportion of fibre surface area prevented from forming bonds by the presence of the filler.  $x$  is dependent on both the filler content,  $L$ , and the filler parameter  $t$ , and subject to the constraints that when  $L = 0$ ,  $x = 0$ , and also that when  $L = 1$ ,  $x = 1$ , because as the fibre content approaches zero, all of the fibre surface area will be covered by filler.

In order to account for fillers of different densities, including hard aggregated fillers in which the effective density of the aggregate is much less than the skeletal density of the mineral, we use the ratio of the volume fraction of the filler particles or aggregates,  $V_m$ , to the volume fraction of the fibres,  $V_f$ , in place of the mass fraction  $L$ . We determined empirically that the function

$$\frac{T_L}{T} = \frac{1}{1 + \frac{aV_m}{tV_f}} \quad (8)$$

fits the shape of plots of tensile strength vs filler content very well for a wide range of studies, and also meets both of the constraints described above. From the gradient of Bown's graph of the filler content required to reduce the sheet tensile strength/unit fibre mass by 30% as a function of  $t$ , the constant  $a$  must have a value of approximately 10, and to be dimensionally consistent it has units of  $\mu\text{m}^{-1}$ .

Although equation 8 was determined empirically according to the criteria outlined above, we can see that it has the same form as the relationship derived by Beazley (equation 3) if, as shown, the constant  $c$  can be neglected. The latter equation can be rearranged to

$$\frac{T_L}{T} = \frac{1}{1 + \frac{TS_m L}{k(1-L)}} \quad (9)$$

If  $L$  is replaced by the volume fraction of filler  $V_m$ , then this is equivalent to equation 8, but with different constants. Beazley derived his expression assuming that, in the areas of fibre contact, fibre/fibre bonds are replaced by weak filler-filler bonds, and that the amount of replacement is proportional to the amount of filler and its surface area. If we assume instead that the filler simply eliminates fibre-fibre bonds instead of replacing them with filler-filler bonds (so therefore  $b_m$  in equation 2 is zero), and that the amount eliminated is proportional to  $1/t$ , then equation 8 can be derived by the same analysis.

## THE EFFECT OF MICROFIBRILLATED CELLULOSE ON SHEET STRENGTH AND LIGHT SCATTERING

In recent years, there has been much interest in the use of micro- and nano-fibrillated cellulose (mfc and nfc, respectively) to enhance the strength of paper [21,22]. There are many ways of making these materials [23,24,25], but all aim to separate fibres into their constituent fibrils. Coarser versions are generally called mfc and made mainly by purely mechanical methods, such as multiple refining, grinding, microfluidisation or homogenization. Chemical pretreatments such as enzyme hydrolysis, carboxymethylation and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) - mediated oxidation facilitate the separation of fibrils and usually result in a finer material after mechanical disintegration, which we shall refer to as nfc. Ahola et al. [26] made nfc by carboxymethylation followed by microfluidisation and studied its effect in paper. In order to incorporate it into the sheet, they used a poly(amideamine) epichlorohydrin (PAE) polymer either to bind the nfc directly to the fibres or to make aggregates that could be retained easily. The nfc was much more effective when bound to the fibres, and improvements were attributed to the increase in fibre-fibre bonding achieved by the nfc and the PAE, but the authors did not speculate on whether the nfc increased bond strength or RBA or both. Eriksen [27] made mfc either by grinding or homogenisation at various energy levels and added it to unfilled thermomechanical pulp (TMP), which showed that it reduced the sheet light scattering and increased its strength (thus presumably increasing the RBA). The mfc became increasingly more effective as the fibril size decreased. Taipale et al [28] made both carboxymethylated nfc and untreated mfc, and added it to an unfilled bleached softwood Kraft furnish. They observed increased tensile strength and Scott bond, which they attributed to increased RBA, although they did not measure light scattering. Guimond [29] mixed TEMPO-oxidised nfc with ultrafine kaolin to aid its retention and added it to refined and unrefined Kraft pulp and TMP. Strength improvement was seen when the nfc was added to the unrefined Kraft and the TMP, but not when it was added to the refined Kraft. The authors suggested that nfc can fill in the voids between fibre and filler and improving fibre/filler contacts. Gonzales et al [30] added TEMPO-oxidised nfc to unfilled Kraft handsheets at various degrees of refining. They found that addition of sufficient nfc to unrefined sheets to match the tensile strength of refined sheets gave similar burst and tear strength, but higher opacity, lower porosity (air permeability) and much slower drainage. Hii and co-authors [31] studied the addition of mfc, made by multiple homogenizer passes, and calcium carbonate filler to TMP sheets, and concluded that the mfc could wrap around filler particles and bond them effectively to fibres.

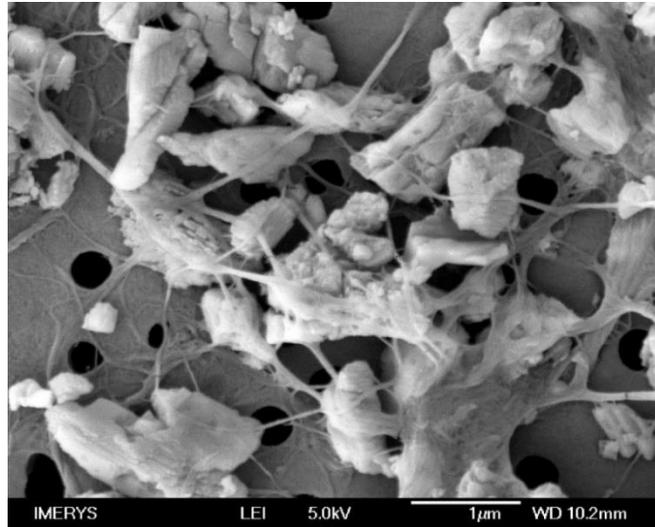
Su and Batchelor [32] added mechanically-produced mfc to unrefined eucalyptus Kraft pulp over a range of levels up to 75% by weight. They plotted tensile strength against sheet density and compared it against sheets made from the same pulp at various degrees of refining in a PFI mill up to very high energy (10000 revolutions). Addition of mfc at up to 10wt% gave significantly higher strength at a given density than moderate levels of refining, but at the highest densities, which required mfc addition levels greater than 50% or very high refining energy, strengths were comparable. The authors concluded that the bond strength between fibre contacts must be similar in both cases, and that low levels of mfc increase RBA rapidly. They also noted that sheet porosity was lower at all density levels with mfc addition. Furthermore, the mfc gave much higher wet

strength (i.e. strength after drying and re-wetting) than refining. They attributed these differences in part to the higher aspect ratio of the mfc than the fibres, which they estimated using a combination of electron microscopy and sedimentation height measurements. Finally, they concluded that refining at high energies produces tethered microfibrils giving the same strength as addition of free mfc, but faster sheet drainage since the tethered microfibrils cannot migrate into the sheet pores and block them.

Our own process for the production of mfc involves the co-grinding of pulp fibres and mineral particles in a stirred media mill. The mineral particles are an integral component of the grinding process, and the product is an intimate mixture of the mineral and the mfc. The material has been run successfully on many different papermachines [33]. It is typically added to paper at concentrations of 1-4% to increase tensile, tear and surface strength, reduce permeability and allow a substantial increase in filler content.

## **EXPERIMENTAL DETAILS**

We have carried out a detailed handsheet study to evaluate the above analysis and to investigate the mechanism by which mfc increases strength of filled paper. A 70/30 mixture of bleached hardwood/softwood Kraft pulp was refined in a disc refiner at various energies covering the range 500 CSF to 250 CSF, and handsheets were made from the resulting mixtures and added filler grade ground calcium carbonate (Intracarb 60, Imerys: 60% below 2 $\mu$ m, median 1.5 $\mu$ m equivalent spherical diameter by sedimentation) from 0 to 40% by weight. A standard British handsheet former was used, which has been adapted to allow for collection and recirculation of whitewater. For sheets including mfc, a co-ground mfc product made from 50% bleached softwood Kraft fibre and 50% Intracarb 60 was added to the sheet in order to obtain the target mfc level. Additional filler was then added to reach the target total filler content for each sheet. It was thus not possible to make completely unfilled sheets containing mfc: the minimum filler content was equal to the mfc dose in each case. A 0.12 wt% dose of cationic polyacrylamide retention aid (Percol 292, BASF) was added to the furnish for each sheet. Recirculation of the whitewater was used to ensure very high overall retentions of all of the components. For each trial point, 12 sheets were made, and the first six were discarded to ensure that whitewater equilibrium had been reached for all the sheets tested. Filler levels were determined by ashing at 450°C; in all plots of properties *vs.* filler content, the measured levels are shown. In each case, the filler content of the sheets matched the filler content added to the furnish to within 1%, so that, for example, if 40% filler was added to the furnish, the tested sheets contained at least 39%. Whilst it was not possible to measure the mfc content of the sheets, previous comparison of single pass and recirculated sheets has indicated that mfc retention is generally higher than filler retention, so we are confident that the sheets made for this study contain the target amounts of mfc. Sheets were pressed, dried on a laboratory drum drier and conditioned at 23°C and 50% RH overnight prior to testing.



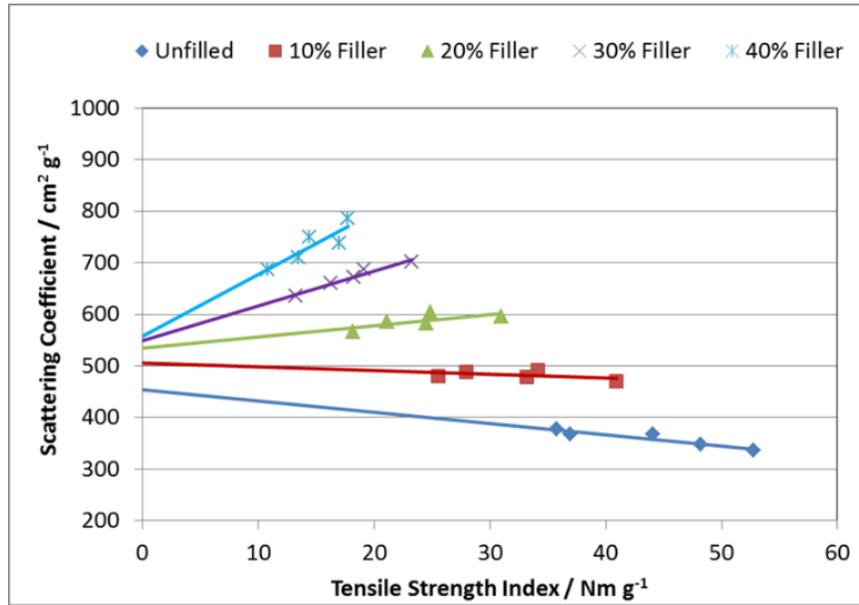
**Figure 2.** Mixture of microfibrillated cellulose and mineral particles produced by the co-grinding process

Measurement or estimation of the size and aspect ratio of the mfc fibrils in the co-ground product is extremely difficult, because the fibrils will easily form a web structure, and the separation of fibres into fibrils by the process is incomplete (Figure 2). Extensive electron microscopy analysis of products made from the same starting materials and by the same process as the one used in the current study gave a number-average median fibril diameter of around 30nm, but the same analysis gives a similar value even for lightly refined pulp, because in each case the number of fibrils is vastly greater than the number of fibres. It is not possible to locate the ends of the fibrils in microscope images, so a reliable estimate of length or aspect ratio could not be made. However, some assumption about the length of the fibrils is necessary if the number distribution by diameter is to be converted into a volume distribution. Assuming arbitrarily that the fibrils and fibres all have an aspect ratio of 100, the median fibril diameter by volume is approximately 3  $\mu\text{m}$ , compared with a value of 30  $\mu\text{m}$  for the starting pulp. This confirms that the mfc used in this work is considerably coarser than the chemically pretreated nfc materials used in many of the other studies cited [26,28,29,30]

## RESULTS AND DISCUSSION

### Sheets without mfc addition

Figure 3 shows the light scattering coefficient of sheets without mfc addition as a function of their tensile strength, and clearly demonstrates that at high filler levels, both light scattering and strength increase with higher levels of refining as Bown [13] showed.



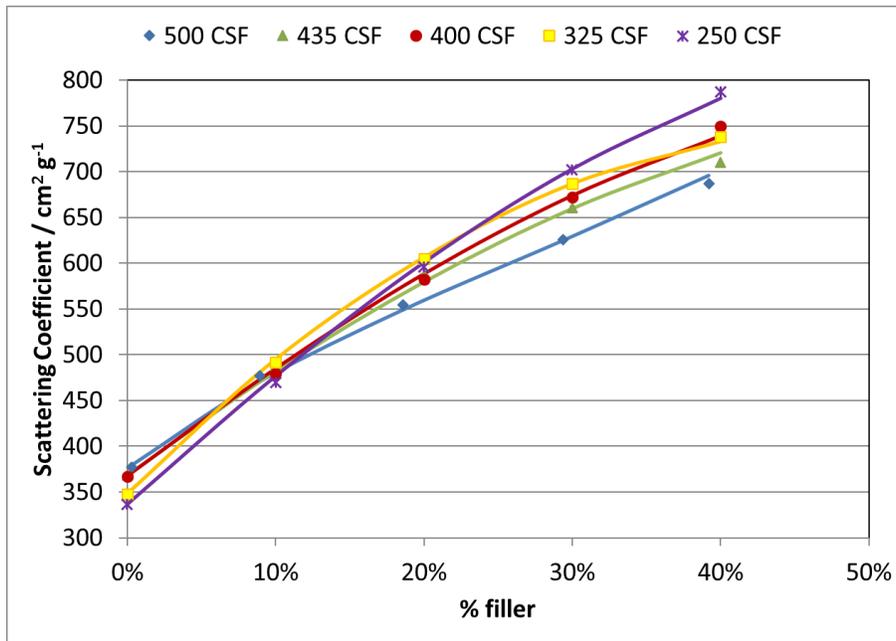
**Figure 3.** Light scattering vs. tensile strength as a function of refining. Handsheets made from 70/30 hardwood/softwood and filler grade ground calcium carbonate

Using these data, we determined values for all of the parameters in the model described in the previous section.  $S_0$  was determined from the extrapolation of the graph of tensile strength vs. light scattering for the unfilled sheets as described earlier. To obtain a single value for  $S_{filler}$ , Bown [13] extrapolated lines of sheet light scattering coefficient vs. tensile strength at constant filler loading (equivalent to those in Figure 3) back to zero strength, on the assumption that at this point there is no contribution to the scattering from the fibrils, and thus the total scattering reduces to

$$S_{zero\ strength} = (1 - L)S_0 + LS_{filler} \quad (10)$$

He thus plotted  $S_{zero\ strength}$  against filler loading to obtain  $S_{filler}$ . For this study, we determined the optimum value for  $S_{filler}$  by a different method, to reduce the dependency on extrapolations. We obtained a single value of  $S_{filler}$  and values of  $S_{fibrils}$  at each refining level by a fitting procedure, in which the total scattering (i.e. the sum of equations 5, 6 and 7) was calculated and the values of

these parameters adjusted to give the best overall fit to the data. The tensile strength per unit fibre mass of each filled sheet relative to the unfilled sheet at the same refining level,  $T_L/T$ , was taken directly from the tensile measurements in each case. The results of the fitting procedure are shown in Figure 4. For the filler grade calcium carbonate used,  $S_{filler}$  was determined to be  $1050 \text{ cm}^2 \text{ g}^{-1}$ , very close to the value determined by Bown for a filler grade kaolin ( $1000 \text{ cm}^2 \text{ g}^{-1}$ ). Note that the curves cross at a filler content between 10% and 20%; this corresponds to the transition in Figure 3 from a negative to positive gradient, where increased refining begins to increase rather than decrease the total light scattering from the sheet.

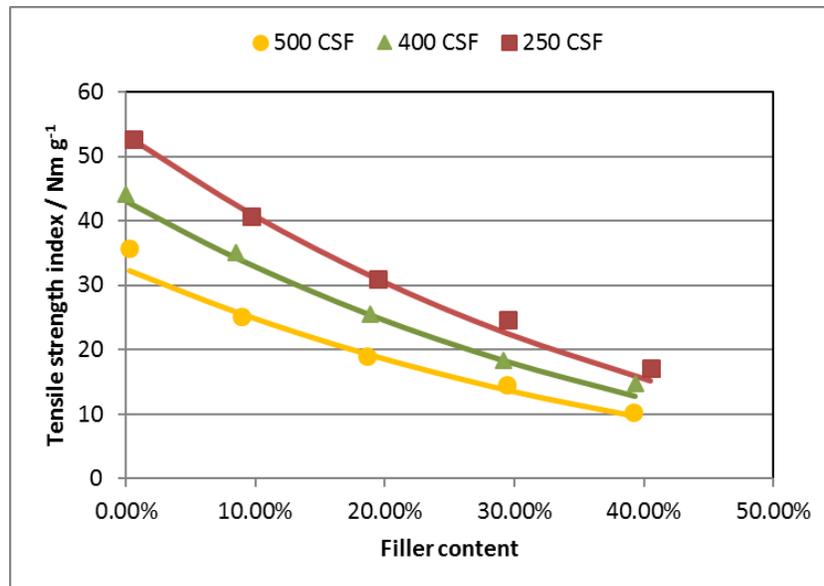


**Figure 4.** Curves of scattering coefficient vs. filler content and theoretical fits (solid lines) used to determine  $S_{filler}$  for the filler grade calcium carbonate.

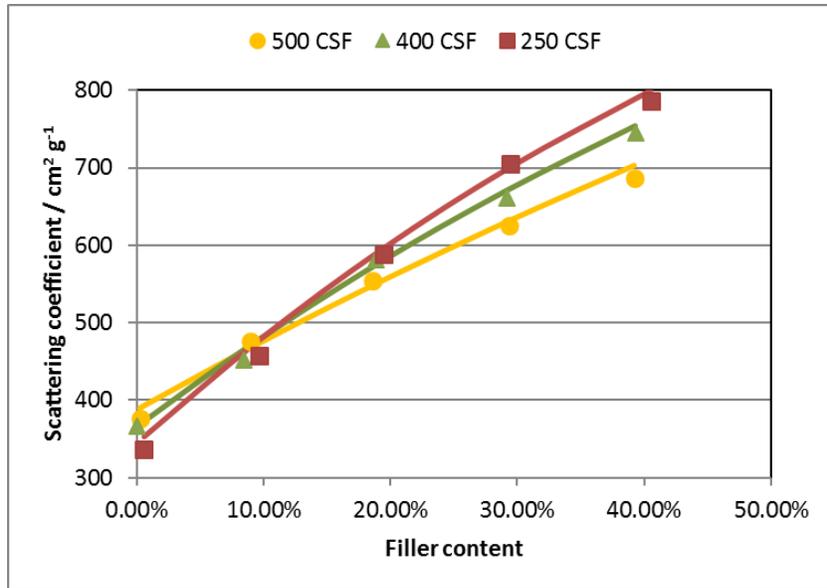
To determine the optimum value of  $t$  for the calcium carbonate filler used, we used a similar fitting procedure, in which its value was optimized to match the data of tensile strength vs filler loading at the lowest refining energy to equation 8. The constant  $a$  in the equation was fixed at a value of  $10 \mu\text{m}^{-1}$  in order to match Bown's plot [16] of the filler loading required to reduce strength by 30% as a function of  $t$  for a range of different filler types. This gave a value of  $3.6 \mu\text{m}$  for  $t$ , in good agreement with his values of  $3.0 \mu\text{m}$  for a standard filler kaolin and  $4.0 \mu\text{m}$  for a slightly coarser filler chalk.

The parameters  $S_0$ ,  $S_{filler}$ ,  $a$  and  $t$  are not dependent upon filler level or refining, and thus have the same value for all of the calculations shown. However, the parameters  $A$  (the RBA of the unfilled sheets) and  $S_{fibrils}$  are both dependent upon the refining level used. A single value for the relationship between the tensile strength per unit fibre mass and  $A$  for this pulp was taken from the gradient of the plot of light scattering vs. tensile strength for the unfilled sheets used in the

determination of  $S_0$ . To complete the comparison of the handsheet data with the theoretical model described, values  $A$  and  $S_{fibrils}$  were optimized using the measurements of strength and light scattering vs. filler content at each refining level, with the ultimate aim of determining whether the effects of addition of mfc shown later can be described using the same approach. Solid lines in Figure 5 and Figure 6 are generated entirely from the model with the optimized parameters, and show that it gives good agreement with the measurements. Note that the values of  $S_{fibrils}$  are slightly different compared with those used in the fits shown in Figure 4, since here the scattering is calculated using the strength values from the model rather than the measured values, in order to make the model entirely self-consistent. Both the unfilled bonded area fraction,  $A$ , and the scattering coefficient due to uncollapsed fibrils,  $S_{fibrils}$ , increase with refining as expected (Table 1).



**Figure 5.** Tensile strength vs. filler content (points) and theoretical fits (solid lines)



**Figure 6.** Light scattering vs. filler content (points) and theoretical fits (solid lines)

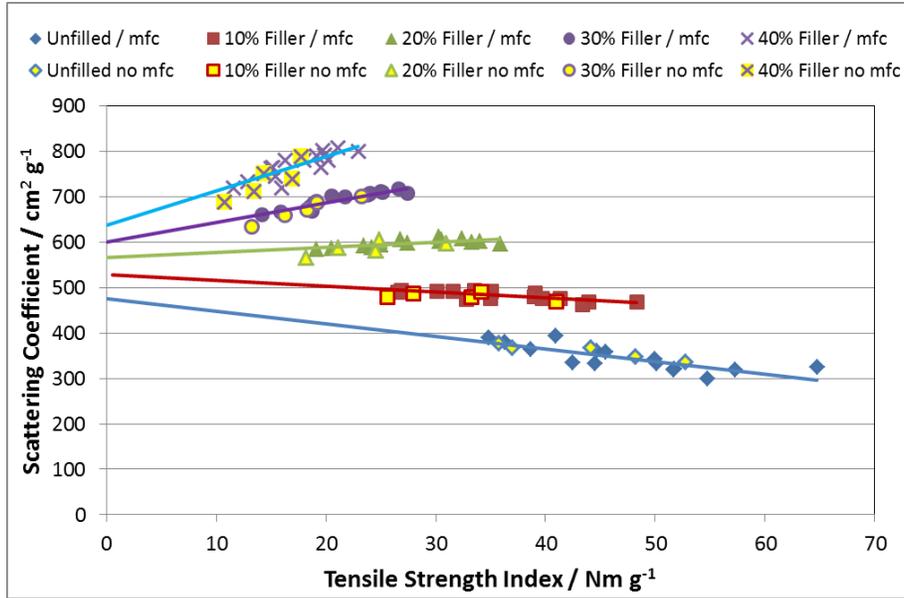
| Parameter     | 500 CSF | 400 CSF | 250 CSF |
|---------------|---------|---------|---------|
| $A$           | 0.146   | 0.193   | 0.241   |
| $S_{fibrils}$ | 630     | 910     | 1116    |

**Table 1.** Variable parameters used in theoretical fits shown in Figure 5 and Figure 6

### Sheets with mfc addition

Sheets containing the co-ground calcium carbonate/mfc product were made using the same procedure as described above, with the same refining conditions and the same total filler contents. Fixed levels of mfc from 0 to 4% were targeted, so that there was a small filler level derived from the mfc product equal to the mfc content in each sheet, and the rest of the filler was added as before to reach the total. In the many studies and trials we have carried out, we have seen no evidence that the co-grinding process affects the filler particle size distribution of this grade, so we consider the filler from the two sources to be equivalent.

Figure 7 is a plot of light scattering vs. strength at different filler levels for all of the sheets in the study, both with and without mfc addition. The addition of the mfc appears to increase strength and change light scattering in a similar way to increases in refining, and it is notable that all of the points lie approximately on the same lines of constant filler level whether mfc is present or not. It thus appears that the effect of addition of mfc is both to increase the bonded area and to increase the light scattering due to uncollapsed fibrils in the same way as increasing the refining level.

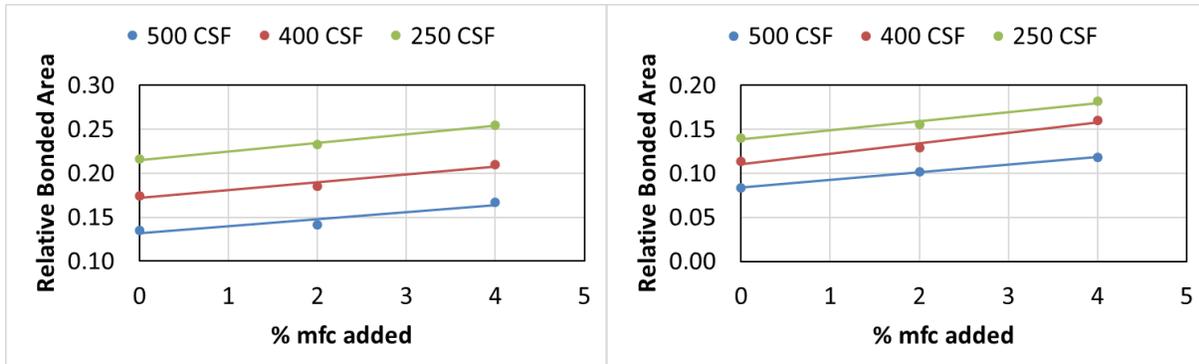


**Figure 7.** Light scattering vs tensile strength for a range of refining levels and mfc addition

The analysis of the sheets with and without mfc addition can be used to estimate the magnitude of the change in bonded area and fibril light scattering coefficient as a function of mfc content. An estimate of the bonded area can be taken directly from the tensile strength per unit fibre mass of the sheets, using the gradient ( $m$ ) of the unfilled plot of tensile strength vs. scattering that was used to determine  $S_0$ , so that in each case

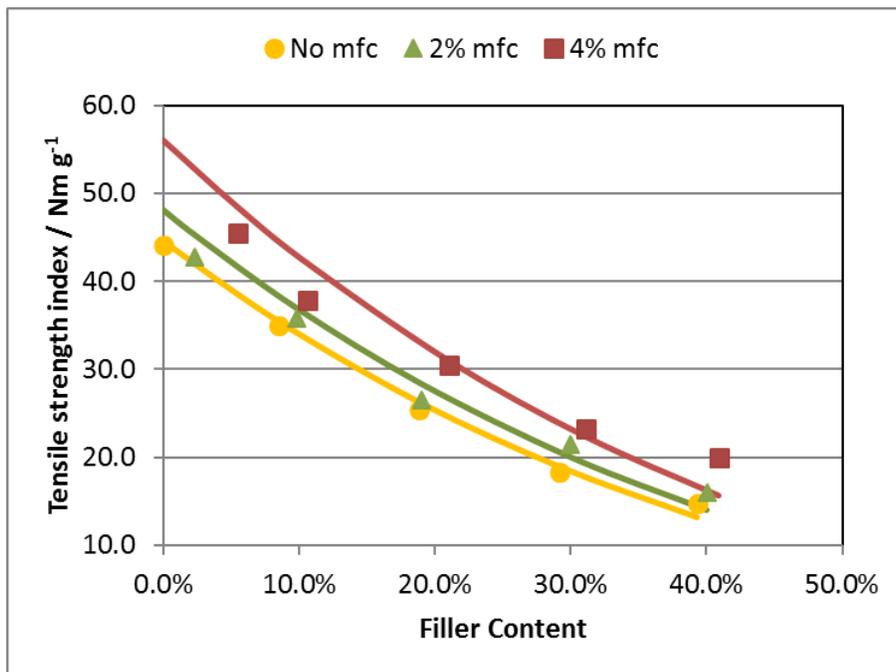
$$A_L = \frac{m}{S_0} T_L \quad (11)$$

The analysis indicates that mfc increases the bonded area of the filled sheet by a fixed amount that is linearly proportional to the added amount, and independent of refining level (Figure 8). The relative effect of the mfc is therefore higher at lower refining levels, because there is less bonded area to begin with. Note, however, that the gradients of the lines shown in the figure are approximately the same at 10% and 40% filler contents, and in each case the bonded area increases by approximately 1% for every 1% of mfc added. In contrast, an increase in refining energy increases the bonded area more at low filler levels than at high filler levels, as can be seen by the fact that the lines are closer to each other at 40% filler than at 10% filler. The filler therefore appears to be less disruptive to bonding resulting from mfc addition than it is to bonding resulting from refining.



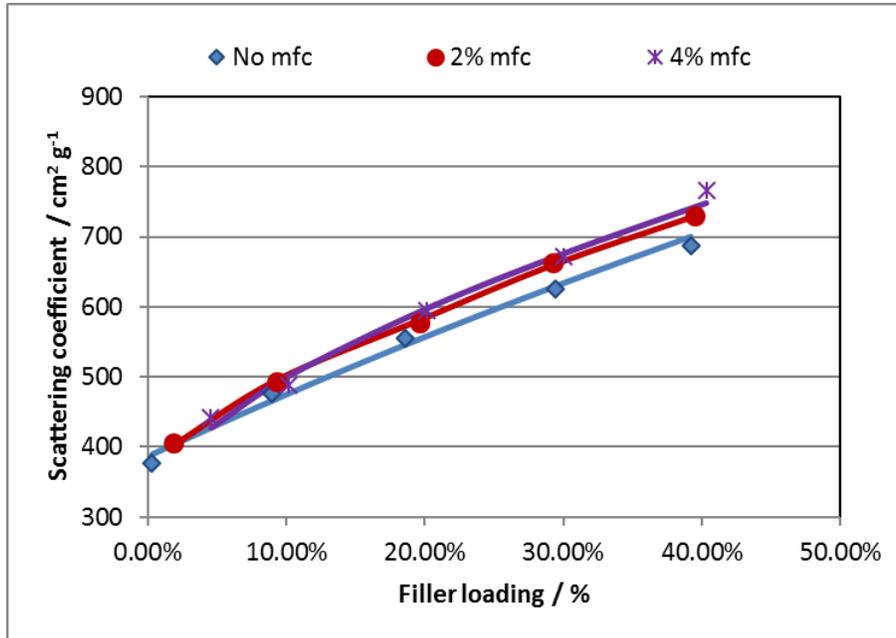
**Figure 8.** Calculated relative bonded area at 10% (left) and 40% (right) filler content as a function of MFC addition level

This is further illustrated by attempts to fit the strength vs. filler content model to the data from the mfc-filled sheets. With the bonded area in the unfilled sheet,  $A$ , and the fibril scattering coefficient  $S_{fibrils}$  as the only adjustable variables, a good fit to the data from the mfc-filled sheets is not possible, since it overestimates the effect of a high filler content on the sheet strength, as illustrated for the 400CSF pulp in Figure 9.



**Figure 9.** Tensile strength vs. filler content and theoretical fits (solid lines) for mfc addition to sheets made from pulp refined to 400 CSF

The apparent scattering coefficient of the fibrils was also calculated by fitting the Bown model to the handsheet data, using the measured strength data in the same way as for the determination of  $S_{filler}$ . Because the real strength values at each loading are used to determine  $S_{fibrils}$  rather than those derived from the model, fit quality is better (Figure 10). Note that the curves do not cross at around 10% filler as they do for different refining levels in Figure 6. At the low refining level, 500 CSF, the calculated fibril scattering coefficient increases with mfc addition, whereas at higher refining level it reaches a plateau (Table 2).



**Figure 10.** Curves of scattering coefficient vs. filler content and theoretical fits (solid lines) used to determine  $S_{fibrils}$  at 500CSF for different mfc levels

| $S_{fibrils}$ | 500 CSF | 400 CSF | 250 CSF |
|---------------|---------|---------|---------|
| No mfc        | 630     | 910     | 1115    |
| 2% mfc        | 940     | 1230    | 1250    |
| 4% mfc        | 1065    | 1220    | 1210    |

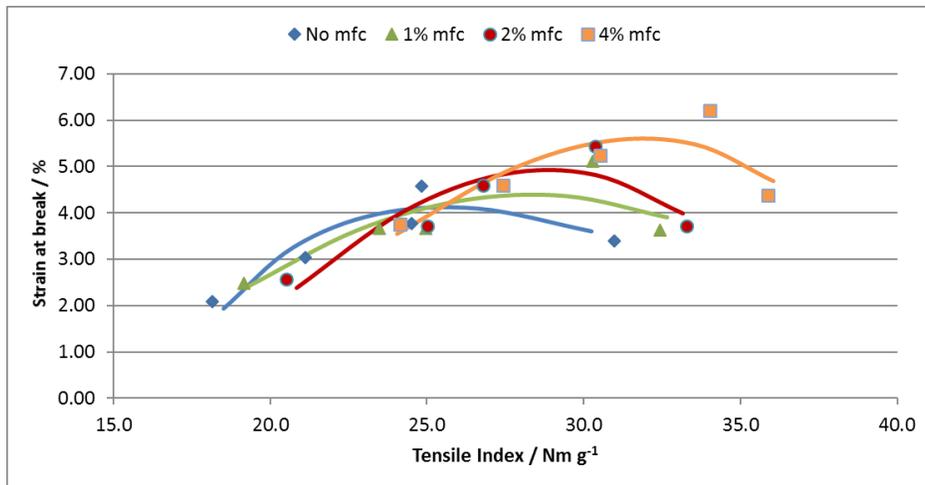
**Table 2.** Fitted values of the light scattering coefficient due to uncollapsed fibrils as a function of refining level and mfc content

The handsheet study shows that addition of mfc to highly filled paper increases strength, and to a lesser extent increases light scattering. Superficially, the plot of tensile strength vs. light scattering in Figure 7 seems to indicate that the effect of mfc is the same as that of refining, since the mfc-containing points lie roughly on the same lines at constant filler level as those derived from different refining levels. However, closer inspection using the Bown model suggests some significant differences. Assuming that the observed strength increase is due to an increase in

bonded area, the effect of mfc addition is to add a fixed quantity of bonded area at all refining levels and filler levels. This area is not disrupted by filler in the same way as increased area from refining would be. Furthermore, there is a limit to the extra light scattering than can be generated by mfc addition compared with that attributed to fibrils with increased refining. This is perhaps indicative that mfc is capable of filling in the voids created by filler particles in the contact areas between fibres as suggested by Guimond for nfc [29], or wrapping around the filler particles and promoting their bonding to and between fibres as postulated by Hii [31] for mfc.

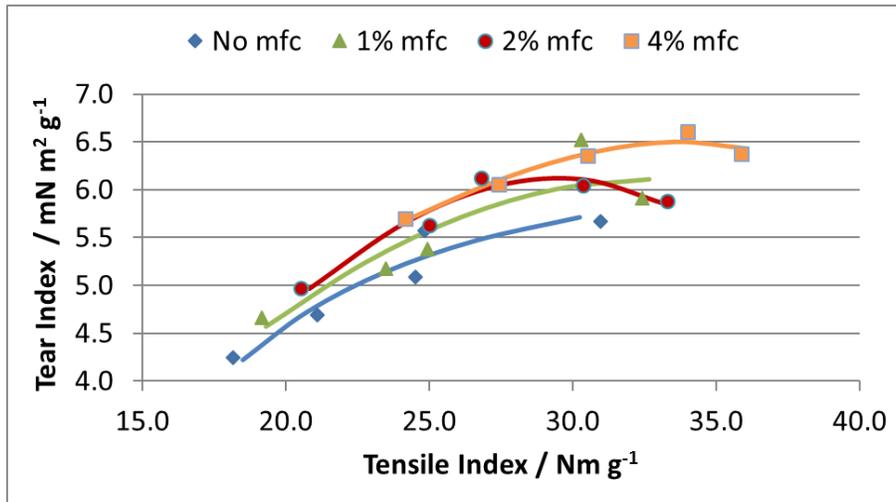
## OTHER EFFECTS OF MICROFIBRILLATED CELLULOSE ON PAPER PROPERTIES

As well as offering a simple and very flexible alternative to increased pulp refining, the addition of mfc also allows the development of properties beyond that which can be achieved with refining alone. For example, data from the handsheet study described earlier at 20% filler content (Figure 11) shows how strain at break initially increases with refining but then begins to decrease as tensile strength rises, whereas it continues to increase with mfc addition. Values of strain 30% higher than the maximum reached with refining can be achieved with 4% mfc.



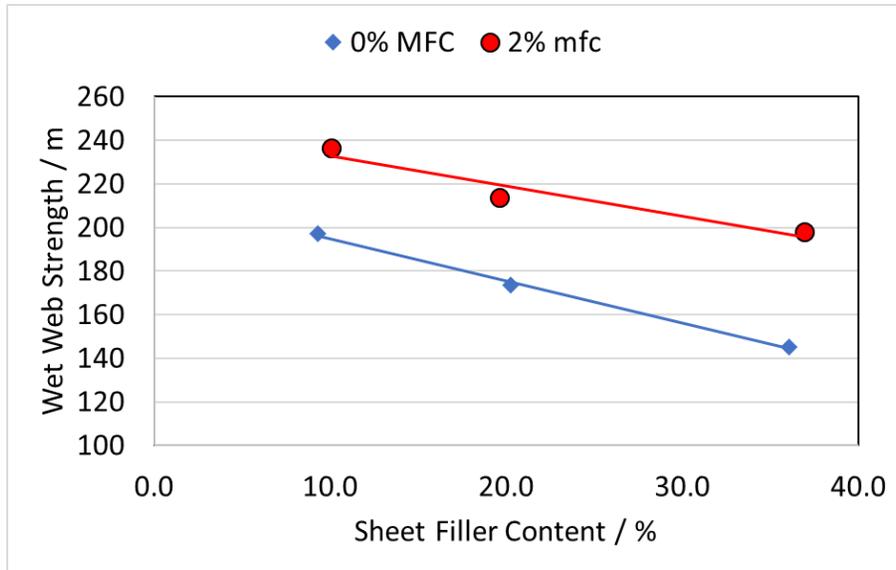
**Figure 11.** Strain at break vs tensile strength at 20% filler content for a range of refining levels and mfc addition

Tear strength also commonly passes through a maximum with refining, though in this study where predominantly short fibre was used it was just reaching a plateau at the lowest freeness achieved. Nevertheless, Figure 12 shows that addition of mfc gives a greater increase in tear strength than can be achieved by increasing refining to the same tensile value.



**Figure 12.** Tear strength vs tensile strength at 20% filler content for a range of refining levels and mfc addition

Although the addition of mfc can slow down initial dewatering as the paper web is formed, this is typically compensated by the desired increase in filler content and subsequent reduction in fibre. It has also been relatively simple to adjust dewatering using retention/drainage chemicals and reducing the initial water content of the pulp slurry. In several pilot trials, we have measured the strength of the wet web after the press section, and shown that the effect of mfc on this property is significantly larger than its effect on dry strength. Figure 13 shows data from a recent trial; at 20% filler content the wet web strength (expressed as a breaking length in m) is about 25% higher with the addition of 2% mfc, and in this particular case the 2% mfc addition gave equivalent wet web strength at 35% filler as was observed at 10% filler without it. As mentioned earlier, Su and Batchelor [32] noted that addition of high levels of mfc to handsheets had a much greater effect on wet strength than on dry, although crucially their measurements were on strength after rewetting, whereas here we measure strength before drying. We also observed that in this trial the solids after the press were approximately equal at 10% filler loading, but surprisingly were somewhat higher with the mfc addition at 35% filler loading. This is consistent with our experience using mfc in full scale production, where in most cases the papermaker has been able to increase filler levels beyond what would be predicted from dry sheet properties alone.



**Figure 13.** Effect of mfc addition on wet web strength measured on a pilot papermachine. Fine paper furnish, 20% filler grade calcium carbonate.

## CONCLUSIONS

The addition of microfibrillated cellulose to paper has been shown to increase tensile strength and, to a lesser extent, light scattering, in highly filled papers. The relationship between the two is superficially similar to that seen with increased levels of refining, although it appears that the effect of mfc on tensile strength is more significant at high filler content. We attribute the increase in strength to an increase in bonded area, where the area added is proportional to the mfc dose, and is less susceptible to disruption by filler than the bonded area generated by refining. At equivalent strength levels, mfc addition has significant advantages over refining, typically including better tear strength, strain at break and wet web strength. Since it is an additive used at only a few per cent, it offers a more flexible approach than variation of the refining energy of the whole fibre furnish.

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