Using thin-crystal engineered kaolins to enhance mechanical properties of coatings

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Using thin-crystal engineered kaolins to enhance mechanical properties of coatings.

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ABSTRACT

Structures in nature display hierarchical features which span nano to macroscopic length scales. In paper coatings, the mineral pigment particles themselves form the building blocks, and together with the binder are the limiting factor in determining the structural properties of the coating. The mechanical properties of paper coating layers are very important in converting and printing operations. These include stiffness, resistance to fold cracking, dusting and pick resistance. In this work, we show the potential gains in mechanical properties (such as elastic modulus, tensile strength and stiffness) which can be realised by reducing the z-direction size of the building blocks to nanoscale dimensions. This can be done using kaolins having thinner crystals than have been mined hitherto. For a given coat weight, compared to conventional clays or carbonates, these thin particles give greater energy transfer under tensile deformation and so increase the elastic modulus of the coating layer. This leads to gains in sheet stiffness which allow savings in raw material and energy costs. A coating layer containing thin crystal clay has an elastic modulus 7-8 times higher than one containing only ground calcium carbonate. Future developments in binder design need to be pursued to further improve the modulus of the coating and accelerate dematerialisation of the sheet.

INTRODUCTION

Current research into novel material structures frequently takes its inspiration from nature. For example, aligned platelet structures which mimic nacre have recently been made in the laboratory. Initial success was achieved using PVA-montmorillonite films prepared by layer by layer deposition (LbL) techniques [1]. Subsequent cross-linking achieved tensile strength values in the region of 400 MPa. LbL techniques are not practical industrially, but a more practical approach was taken by Walther et al. [2] who prepared montmorillonite – PVA layers using blade coating. The PVA is first chemisorbed onto the clay surface, the excess removed by centrifugation, and the resulting suspension blade coated onto paper. Sufficient shear induced ordering of the platelets took place, and films having a modulus of 25 – 40 GPa were produced depending on cross-linking.

In paper coating, this kind of approach has potential applicability in the growing area of recyclable barrier coatings. Among traditional coated paper grades, stiffness is a critical property since it limits the amount of dematerialisation that can be achieved for a given grade of paper. It is interesting that reduction of basis weight from 30 to 28 lb ream^{-1} for a major US title was unsuccessful because the magazine had an "insubstantial feel" [3]. Applying a coating layer of high modulus offers a way of increasing coated paper stiffness and enabling the amount of fibre to be reduced. This is desirable for cost and environmental reasons. However, montmorillonite is not a suitable coating pigment in these applications for reasons which include optical properties, such as poor colour and low light scattering, very low coating solids, and the requirement for a porous coating layer to give controlled ink setting.

Kaolin is a widely used coating pigment in the graphic sector, generating good light scatter and porosity, especially in combination with calcium carbonate. Traditionally, coating kaolins have been selected for fluidity, so that coating solids can be high. Inevitably, this means that the kaolin particles have a low aspect ratio. Recently, a new generation of high aspect ratio coating kaolins has been produced from secondary deposits in North America. These particles have large plate diameters but very low plate thicknesses (Figure 1). In the case of the highest aspect ratio fine clays, the crystals approach nanoscale dimensions, <50 nm, Figure 2, values calculated from equations published by Jennings and Parslow [4]. These approach the length scale at which unusual strength properties become apparent due to the avoidance of crack propagation [5]. The micrograph in Figure 3 shows an example of a thin crystal kaolin in a paper coating.

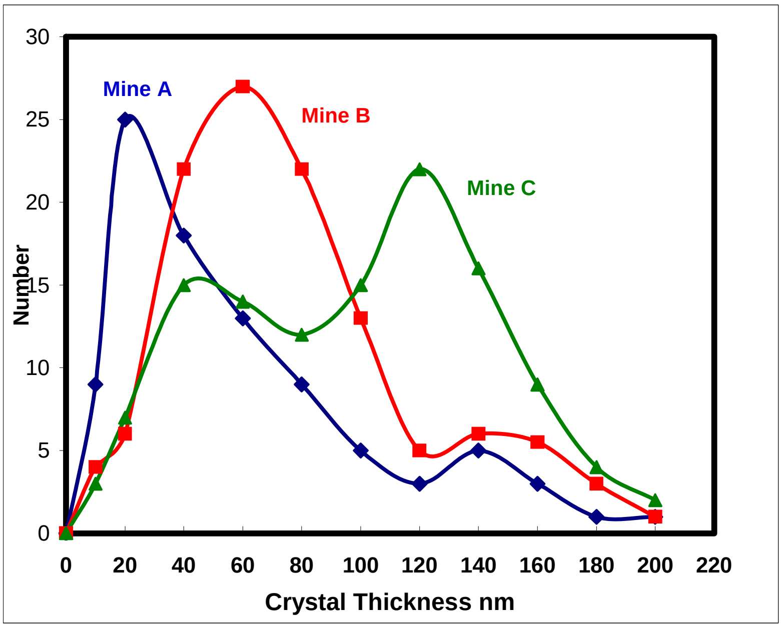

Figure 1. **Thickness distribution of kaolin crystals from different mines in Georgia, measured by electron transmission. Source : R.Pruett.**

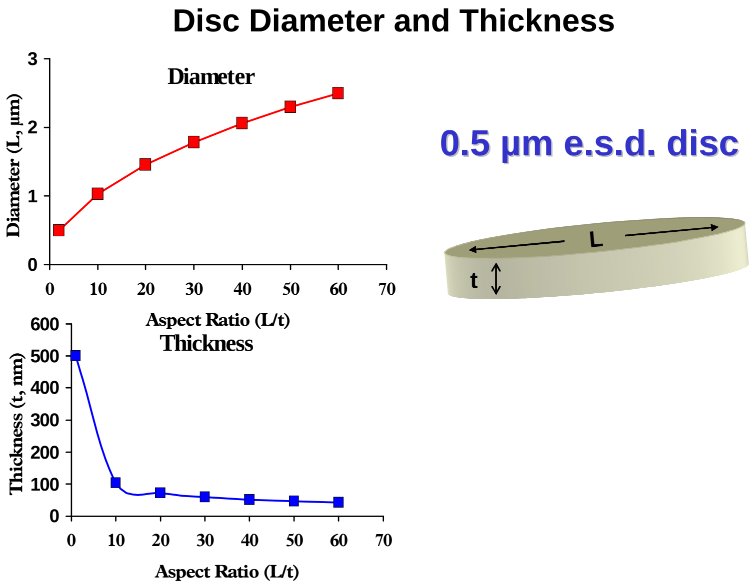

Figure 2. **Disc diameter and thickness values as a function of aspect ratio. Calculated for particles of 0.5 µm esd using the Jennings and Parslow equation [4].**

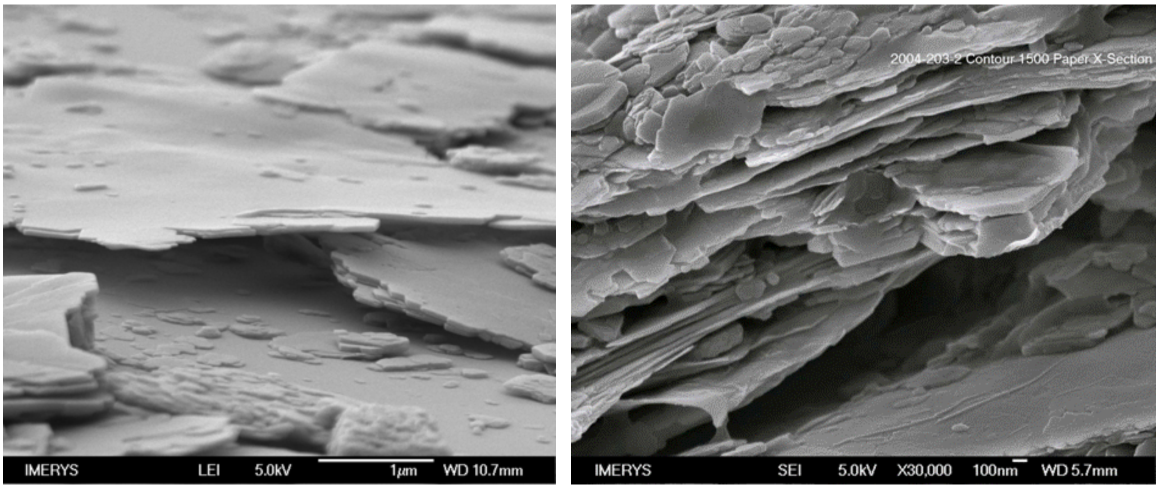

Figure 3. SEM showing thin kaolin plates (left), and in a paper coating (right).

Parpillon *et al.* [6] measured the tensile strength of coating layers based on kaolin and calcium carbonate (GCC). They found that, at the same latex level, kaolin gave coating layers with about twice the tensile strength of GCC. Kaolin also gave greater stiffness. Subsequently, Lepoutre and Rigdahl [7] examined a wider range of pigments of different shape and related the in-plane elastic modulus of coating layers to the presence of voids. Further studies of the z-directional strength of kaolin and GCC layers were reported by Inoue and Lepoutre [8]. They concluded that coating layers based on plate-shaped clay particles were more resistant to in-plane stresses than isometric GCC.

Recently, some work has been published on z-directional coating strength of paper using a micro-indentor [9]. Although applied to coated paper the technique is in an early stage of development; the z-direction elastic stiffness estimated from the indentor showed order of magnitude agreement with that calculated from in-plane tensile measurements for coating layers containing calcium carbonate. For clay, the z-direction result was lower than the in-plane, which the authors suggested might arise as a result of the aspect ratio of kaolin particles.

Engineering the particle shape, or aspect ratio, has made kaolin a very versatile coating pigment which confers additional functionality to coating formulations [10,11]. Our previous studies have investigated the effect of kaolin particle shape on the in-plane and z-direction tensile strength of coating layers [12,13] and the printing strength of papers coated with the same pigments [14]. The present study highlights the role of kaolin particle shape in determining the mechanical properties of coating layers, particularly the in-plane mechanical properties which have been shown to influence the bending stiffness and folding resistance of coated paper [15-17].

MATERIALS AND METHODS

Materials

A series of four coating kaolins were used having approximately similar particle size distributions as determined by sedimentation. These were chosen to cover a range of particle aspect ratio values, from blocky to very platy. The mean (D50) particle size was 0.40 µm esd. Additionally, two ultrafine kaolins were included of blocky and platey morphology. These had a mean size of 0.20µm. A GCC of 95wt% < 2µm (Carbital 95™, D50 = 0.50µm) was also used in some experiments. The properties of the kaolins are summarised in Table 1. The mean aspect ratio (defined as the average plate diameter / thickness) was measured by stopped flow conductivity using a patented technique [18]. The shape trends are generally mirrored by the difference between the average size (D50) as measured by sedimentation using a Micromeritics Sedigraph™ and light scattering using a Malvern Mastersizer™ S. The latex binder used was a carboxylated styrene butadiene acrylonitrile copolymer of Tg = 10°C (DL920, Dow).

The kaolins were slurried at the optimum solids using 0.3wt% of a sodium polyacrylate dispersant (CED3546, Ondeo Nalco). The latex was added at levels between 3 and 17 pph based on clay. 0.3 pph of sodium carboxymethyl cellulose (Finnfix 10™, CP Kelco) was also added as a thickener. After pH adjustment to 8.0, the colours were screened through 53µm. In order to remove air bubbles, the colours were centrifuged at 4000 min^{-1} for 10 minutes. In some experiments a hydroxyethyl derivative of corn starch (Penford Gum 280, Penford Products, USA) was used in combination with latex. The starch was cooked at 20% solids at 95° - 100°C for 20 minutes.

Table I. Physical properties of kaolins

Kaolin type	Grade	Particle size distribution by Sedigraph, wt% below					D50 by light scattering (Malvern) µm	Shape factor	BET surface area, m^2g^{-1}
		2µm	1µm	0.5µm	0.25µm	D50 µm			
FB (Fine Blocky)	Blend of Capim DG / Premier	93	81	63	34	0.37	1.46	16	14
FUP (Fine Ultra Platy)	E^{100}	90	77	60	34	0.40	3.1	56	16
UFB (Ultra Fine Blocky)	Astrasheen	100	99	94	68	0.19	0.32	10	27
UFP (Ultra Fine Platy)	Contour Xtreme	97	90	79	53	0.23	1.43	40	24

Experimental Methods

Coating films were prepared by drawdown using wire wound bars. The substrate chosen was a polyethylene terephthalate film of caliper 13µm (Look! Roasting Film, Terinex Ltd.). This was found by Prall [19] to give the easiest separation of the coatings from the substrate. Coatings acceptable for tensile testing were found by experience to require a thickness of at least 50 µm. This was achieved by using a nominally 150 µm wet film thickness wirewound bar (Sheen Instruments, Kingston, UK). Typically, 100µm thick films were produced. Following drawdown and drying with a hot air stream, we found that the majority of pigment binder combinations could be easily separated from the substrate and were sufficiently self-supporting to handle. The exceptions were using 100 % GCC, which gave very fragile films.

For measurement of tensile strength in the plane of the coating, the films were cut into a barbell shape using a template designed for rubber testing. The length of the barbell was 50mm, and the width of the central bar was 4mm. The thickness of the film was measured using a caliper gauge (Messmer) accurate to ±2 µm. The ends were attached via rubber-faced clamps to a tensile tester (Testometric 350, Rochdale). An extension rate of 10 mm min^{-1} was used for the tensile testing. Experiments were carried out at 23°C and 50% RH. Load and elongation at break were recorded for each sample, and an example of the output is shown in Figure 1. The strength was calculated by dividing the load (N) at break by the cross-sectional area of the sample across which the load is applied to give the tensile strength in force per unit area (MPa). 10 measurements were made on each sample, and the mean value calculated. In the following figures error bars signify the standard deviation. The elastic modulus of the layers was derived from the same data by taking the slope of the initial linear portion of the tensile strength / elongation plot as shown in Figure 1.

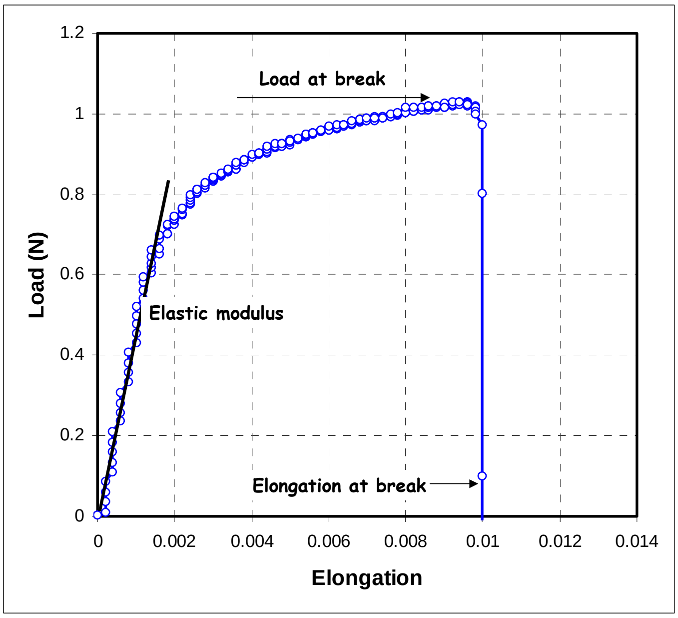

Figure 4. Example of a load / elongation curve for coating (Clay FB / 5pph latex) in the in-plane direction.

Some samples of the coatings were supercalendered using a Perkins laboratory calender. The coatings were placed between sheets of thin lens tissue to avoid the coatings sticking to the rolls. The calender was unheated and the linear load was 78 kg cm^{-1}.

Coated papers were produced on a pilot coater running at 600 m min^{-1}. A 58 gm^{-2} woodfree basepaper was used, and a coatweight of 12 gm^{-2} per side applied using a roll applicator with blade metering. 50% blends of each kaolin were made with a fine GCC (Carbital 95™). 9.5 pph of styrene butadiene acrylonitrile latex (DL920, Dow) and 1 pph CMC (Finnfix 5, CP Kelco) was added throughout. After coating, all of the coated reels were supercalendered under the same conditions using 11 nips with a surface temperature of 100°C and a linear load of 200 kN m^{-1} at 600 m min^{-1}. The moisture of the coated papers was controlled to 5.5 ± 0.3 wt%. Coating and calendering were carried out at the pilot plant at Oy Keskuslaboratorio Centrallaboratorium AB (KCL), Helsinki, Finland.

The bending resistance of the coated papers was measured using a Stiffness Tester (Lorentzen & Wettre), following a SCAN-P test method [20]. 10 measurements of each sample were made, in the machine and cross-machine directions respectively. The results for the two directions were then averaged to give a geometric mean bending resistance.

RESULTS

The effect of particle shape on in-plane properties

Figure 5 shows results for in-plane tensile strength properties of coatings made from all the clays at a range of latex levels. We found that the high aspect ratio clays gave higher in-plane tensile strength than the low aspect ratio clays. The GCC coatings had the lowest in-plane tensile strength, 6-7 times lower than the strongest kaolin, the ultra high shape fine clay.

Figure 6 plots the elastic modulus of the same coatings as a function of latex level. The ranking of modulus values follows that of the tensile strength trends in Figure 5, with the high aspect ratio clays giving the highest modulus values. These high shape clays give a modulus between 5 and 8 times higher than the GCC alone.

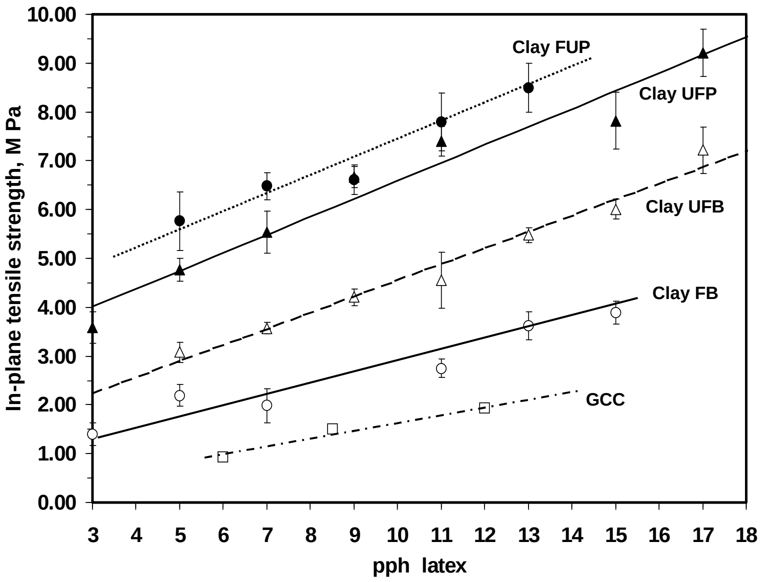

Figure 5. In-plane tensile strength of coating layers as a function of latex level.

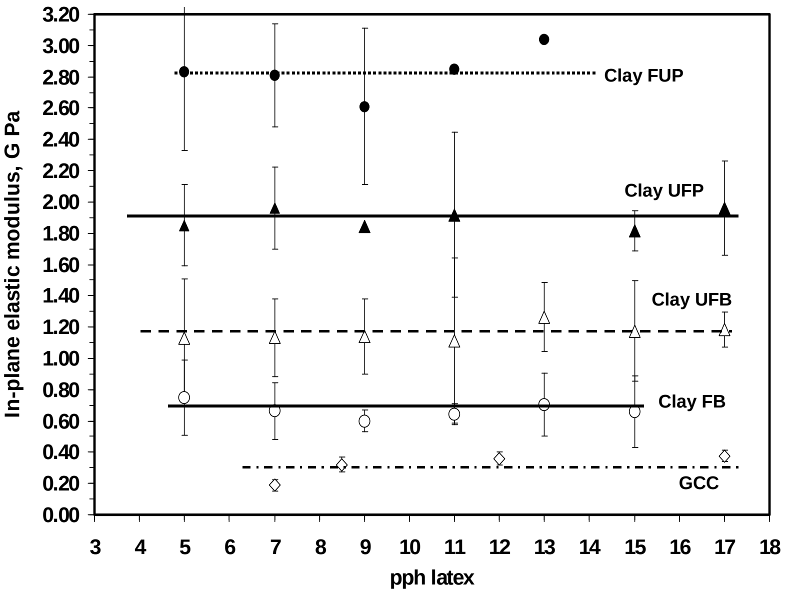

Figure 6. In-plane elastic modulus of coating layers as a function of latex level.

Calendering the coatings based on the ultrafine clays (Figure 7) showed that the in-plane strength and the modulus increased as the coating became denser. After 6 nips the coating layers reduced in caliper by 5-6 %. The platy clay still held the advantage over the blocky counterpart. Also plotted in Figure 4 is the modulus of the basepaper, showing that it is unaffected by calendering. Note that the final modulus values for the calendered coating layer and basepaper are both of the same order of magnitude.

It is also clear from Figures 2 and 3 that the latex contributes to the tensile strength but not the elastic modulus of the coatings. This is in contrast to starch (Figure 8) where we found that substitution for latex leads to an increase in modulus while lowering tensile strength slightly. These trends reflect the known influences of latex and starch on coated paper stiffness, although high modulus latex can be used to build stiffness [21,22,26].

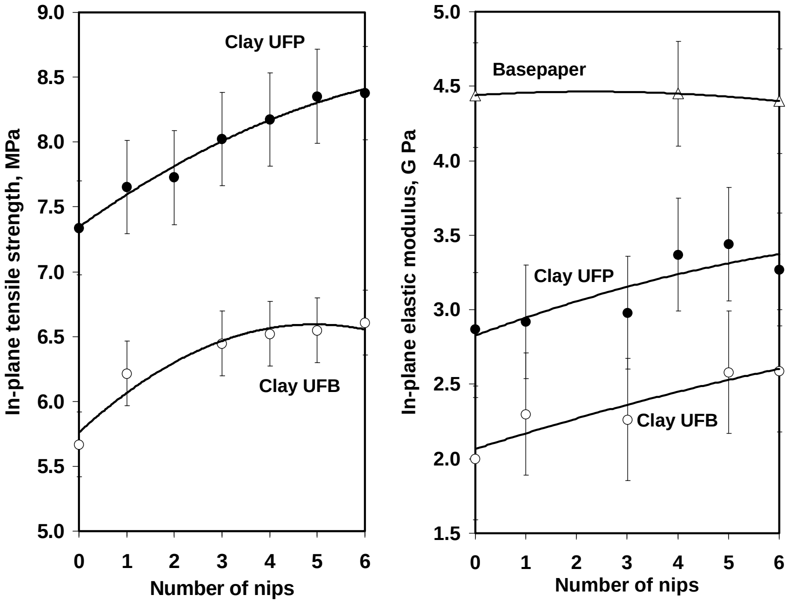

Figure 7. Effect of laboratory calendering of unsupported coating layers and basepaper on in-plane mechanical properties.

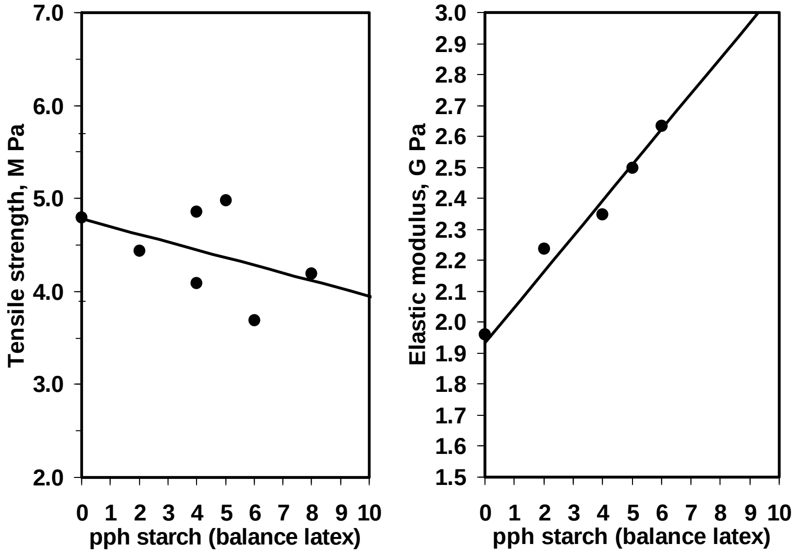

Figure 8. In-plane mechanical properties of coating layers based on UFP kaolin with a latex – starch binder system (total 10 pph).

Blends of kaolin UFP were made with a fine gcc, and the modulus values are plotted in Figure 9. The modulus increases with kaolin addition, but the trend is not linear. These results show that platy clay can have a significant influence on the modulus even at levels of addition below 50 wt%. This is important given that in today's formulations, high carbonate levels are required for good optical properties.

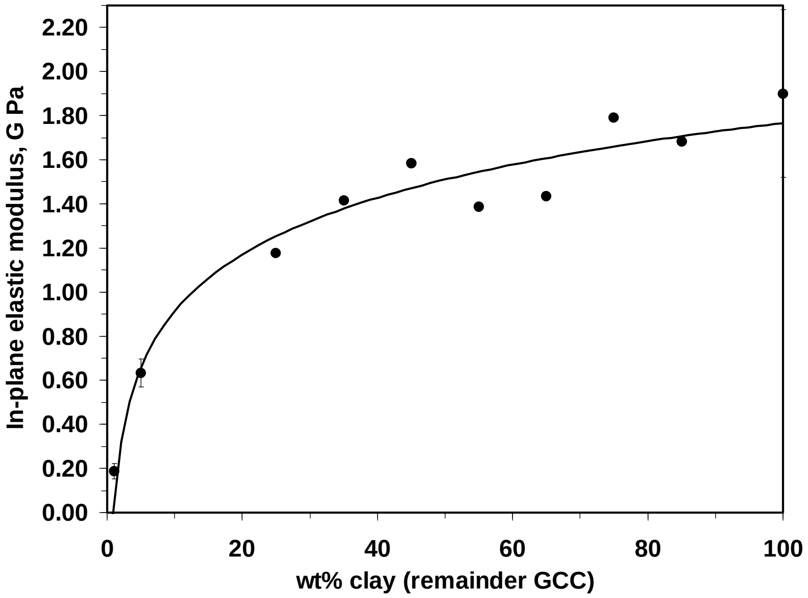

Figure 9. In-plane elastic modulus of coating layers containing kaolin and gcc of different ratios. Latex level 5 pph.

The geometric mean bending resistance values for calendered papers coated with 50 wt% blends of kaolin and GCC from the pilot coating trial are shown in Figure 10. The trends agree with the elastic modulus values plotted in Figure 3, with the fine ultra-platy kaolin giving the greatest contribution to stiffness. We found that there was an excellent correlation between the bending resistance of coated papers containing 50% clay and the elastic modulus values for the coating layers containing 100% of the kaolin component (Figure 11).

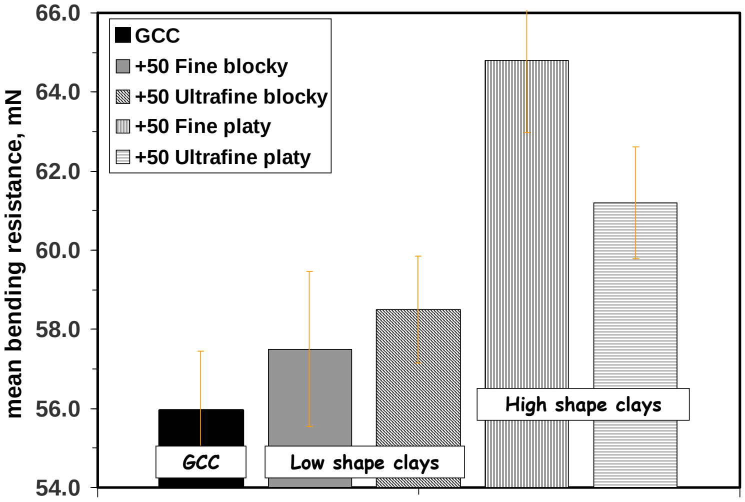

Figure 10. Geometric mean bending resistance of coated and supercalendered papers (9.5 pph latex, 12 gm^{-2} per side).

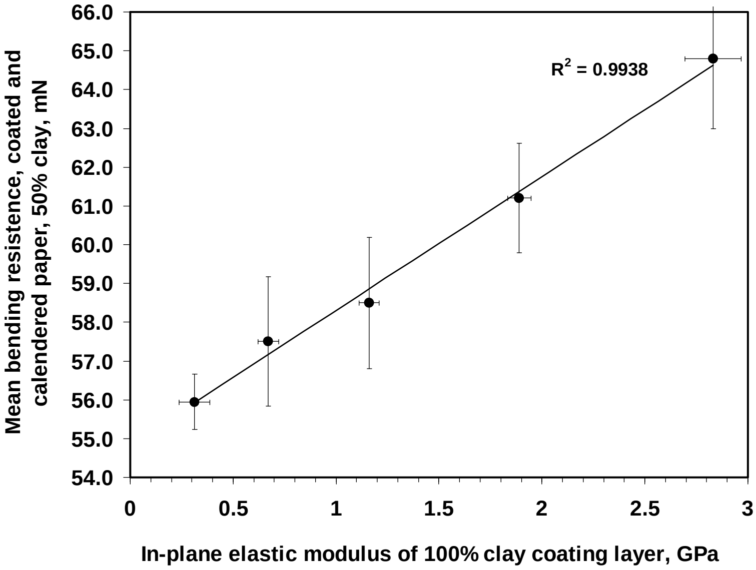

Figure 11. Correlation between geometric mean bending resistance of coated papers and elastic modulus of coating layers.

In turn, there was also a strong linear relation between the mean bending resistance and the shape factor of the kaolin as measured by the method described in [18] (Figure 12).

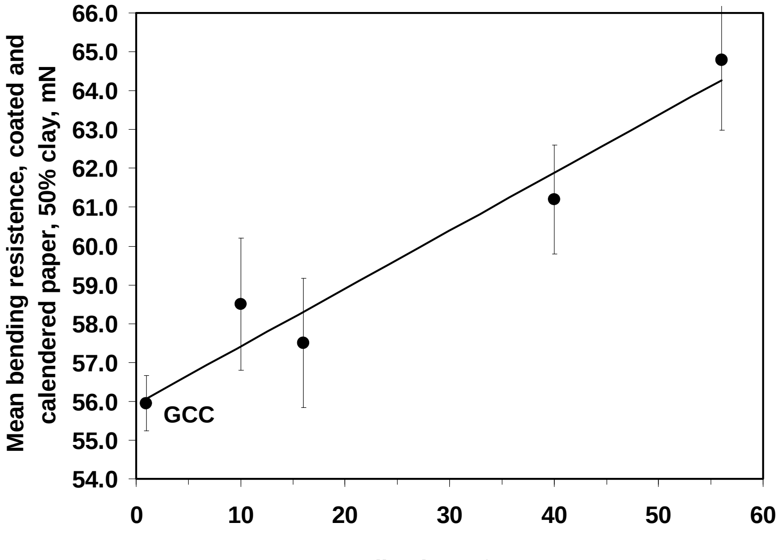

Figure 12. Correlation between geometric mean bending resistance of coated papers and shape factor of kaolin component.

DISCUSSION

This work has shown how the aspect ratio of kaolin particles can be used to influence the mechanical properties of the coating layer. Compared to widely used low aspect ratio glossing clays, high aspect ratio kaolins gave both increased in-plane tensile strength and increased elastic modulus. This advantage of platy clays is also known from polymer science, where platy fillers give enhanced flexural modulus [23,24]. As a result of the increased modulus, we have found that high shape clays are useful in increasing the stiffness of coated papers. Recent studies by Rioux [25] have confirmed these results.

The elastic modulus and the caliper of the paper effectively determine the stiffness of the sheet [27]. The caliper of the paper or the coating layer is critical since it has a third power influence on stiffness. When calendering a coated paper, the stiffness is usually reduced because of the caliper reduction [27]. Our work shows that, after calendering, coating layers increased in tensile strength and modulus, perhaps because the benefits in structure consolidation outweigh the limited reduction in thickness compared to basepapers. High aspect ratio clays still showed a modulus advantage over blocky clays after calendering. Further work should focus on the potential for fold cracking in high modulus coatings, and ways of overcoming this [26].

CONCLUSIONS

The demands for high brightness means that calcium carbonate pigments (ground or precipitated) are an essential component of coated printing papers today. However the isometric particle shape of these mineral particles means that the stiffness contribution from the coating is quite low. We have shown that blending high shape kaolins with GCCs can give useful increases in the stiffness of coated papers. An ultraplaty clay was found to give the largest improvements in stiffness. Blended 50 : 50 with GCC, the bending resistance after calendering was increased by 11 % compared with a blocky glossing clay of similar particle size. Calculations based on published models for multilayer stiffness [27] suggest that this may allow a reduction in basepaper thickness, and thus fibre savings, of around 4 %.

The role of the binder in building the elastic modulus of the coating was also investigated. Increasing the level of a standard SBR latex increased the tensile strength but had no influence on the modulus of the coating layer. Starch was found to increase the modulus of the coating. This is in agreement with the known influences of different binder systems on stiffness of coated paper. It should be noted that high modulus latexes which contribute to stiffness can also be used. Hence a combination of thin crystal kaolin and higher modulus binders, perhaps not yet invented, can build the stiffness of the coated paper and enable further cost savings through reductions in the amount of fibre.

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