A study of in-plane and z-direction strength of coating layers with varying latex content

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A STUDY OF IN-PLANE AND Z-DIRECTION STRENGTH OF COATING LAYERS WITH VARYING LATEX CONTENT

J.C.Husband, J.S.Preston, L.F.Gate, A.Storer† and P.Creaton‡.

Pigments for Paper Group**,** Imerys Minerals Ltd., Par Moor Centre, Par, United Kingdom PL24 2SQ,
†Dept of Chemistry, University of Edinburgh, King's Building, West Mains Road, Edinburgh EH9 3JJ,
‡ School of Chemistry, University of Bristol, Cantock's Close, Bristol, United Kingdom, BS8 1TS.

ABSTRACT

A method to subject a coating layer to tensile deformation in the z-direction has been developed. Results show that using kaolin as the coating pigment, the tensile strength is between 4 and 22 times higher in the in-plane than the z-direction. This is related to the aspect ratio of the kaolin particles, which leads to anisotropic coating properties. High aspect ratio particles give the greatest difference in strength properties with direction. There is an inverse relation between the in-plane and z-direction tensile strength so that as aspect ratio increases, the in-plane strength increases but the z-direction strength decreases. Coatings containing ground calcium carbonate give similar in-plane and z-direction strength properties, confirming the isotropic nature of such coatings.

Application Statement : This study gives insights into important properties of coated papers, especially stiffness and strength and how these might be influenced by the shape of the kaolin particles used. This is important today as basis weights decrease and when mills are demanding the most efficient use of binders.

INTRODUCTION

In the first paper in this series [1], we studied the in-plane tensile strength properties of coating layers based on kaolin and latex. The particle aspect ratio, or shape factor, was shown to influence the in-plane strength, with increasing aspect ratio giving increased tensile strength and stiffness.

We recognise that in-plane tensile is not the only stress vector to which the coating is subjected in use. There are also likely to be z-directional stresses operating at right angles to the in-plane stresses, for example during supercalendering or printing with high tack inks. Given the anisotropic nature of the kaolin-based coating structure, z-direction strength is likely to be different to that determined in-plane. In other words, the coating itself may display anisotropic strength properties. Evidence for this assumption was published by Lepoutre and Hiraharu [2] who investigated the differences in mechanical properties of coating layers based on calcium carbonate and kaolin in the z-direction. Using the IGT pick test with oil, they concluded that the mechanical strength of the GCC coatings was higher than with clay. Using a rolling cylinder technique to measure z-directional strength, they found that the rupture energy of the GCC layer was higher than the clay, and therefore a higher level of binder was required for the clay coating to obtain similar strength to the GCC in the z-direction. Petterson *et al*. also investigated the wet pick strength of coated papers and concluded that GCC coatings were stronger than clay coatings under their experimental conditions [3]. Further studies of the z-direction strength of kaolin and GCC layers were reported by Inoue and Lepoutre [4]. They found that the peel energy of GCC layers was higher than kaolin layers at the same binder level, which in this study, somewhat unusually, was carboxymethyl cellulose.

Recently, some work has been published on z-directional coating strength of paper using a micro-indentor [5], 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 anisotropic nature of kaolin particles. An alternative view was provided by Granier and Sartre [6] who interpreted the strength of coatings in terms of acid – base character of the mineral and latex binder. In their model, the kaolin edges are basic and the faces acidic, so the acidic latex adheres much more strongly to the edges. However, in theory at least, the faces have different chemistry, so this model may be inaccurate. Latex should adhere more strongly to basic $CaCO_3$ than kaolin, but this does not support the published in-plane tensile strength trends. In practice, the presence of dispersant on kaolin particle edge sites or over the whole carbonate surface is expected to influence the adhesion of latex to mineral surfaces. Nonetheless, the effect of surface chemistry on binder – mineral adhesion should form part of any comprehensive theory of coating strength.

Our new study has attempted to measure the tensile strength of coating layers using a similar technique in both directions, so that the anisotropy in the coating layer strength properties can be quantified. Techniques intended to measure the z-direction tensile strength of uncoated papers using an adhesive or tape method to grip the specimen are well established [7-9] but no similar method for coating layers has previously been reported. We have studied these properties as a function of kaolin particle size and shape, as well as mineral type across a range of latex binder levels.

MATERIALS

Two series of coating kaolins were used having approximately similar particle size distributions as determined by sedimentation. These were chosen to cover fine (0.4 µm median size by weight) and ultrafine (0.2 µm median size by weight) particle size ranges. Average aspect ratio (AR) values varied from blocky (AR 10 - 15) to platey (AR 35 - 40). A natural ground calcium carbonate (GCC) of 90wt% < 1µm (D50 = 0.40µm) was also used in some experiments. The pigment properties are summarised in Table I. The mean aspect ratio (defined as the average plate diameter / thickness) was measured by stopped flow conductivity using a patented technique [10]. The aspect ratio trends are mirrored by the difference between the weight average sizes (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 Chemical).

Table I. Physical properties of coating clays used in this study

Pigment	Particle size distribution by Sedigraph, wt% below					D50 by light scattering (Malvern) µm	Aspect ratio	BET surface area, m^2g^{-1}
	2µm	1µm	0.5µm	0.25µm	D50 µm			
Kaolin A	93	81	63	34	0.37	1.46	16	10.5
Kaolin B	90	74	55	31	0.44	1.52	34	15.6
Kaolin C	100	99	94	68	0.19	0.32	10	27
Kaolin D	97	90	79	53	0.23	1.43	40	24
GCC	99	87	56	33	0.40	-	-	21

The kaolins were slurried at the optimum makedown solids needed to impart an energy input of around 15 kWh t^{-1} using 0.3wt% of a sodium polyacrylate dispersant (CED3546, Ondeo Nalco). The latex was added at levels between 3 and 16 pph based on clay. 0.3 pph of sodium carboxymethyl cellulose (Finnfix 10, Noviant) was also added as a thickener. After pH adjustment to 8.0, the colours were screened through 53µm. The addition of some CMC was necessary for good coating application, although it is recognised that its presence may cause some flocculation of the pigment particles. It was found to be important to remove air bubbles, and this was done by centrifuging the colours at 4000 rpm for 10 minutes.

EXPERIMENTAL METHODS

Coating films were prepared by drawdown using wire wound bars. The substrate chosen was a polyethylene terephthalate film (Look! Roasting Film, Terinex Ltd.) of caliper 13µm. This was found by Prall [11] 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 150 µm wet film thickness wirewound bar (Sheen Instruments, Kingston, UK). 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, when very fragile films were produced.

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 development of this method is described in our earlier paper [1]. For z-direction tensile strength measurements, the films were cut into squares 25mm x 25mm and sandwiched between double-sided splicing tapes designed for paper (R9401, Nitto, Belgium). According to the manufacturers, the adhesive is based on a water soluble acrylic polymer. The combination was then inserted between 25mm square stainless-steel specimen blocks (**Fig. 1**) and the assembly placed in an oven at 90°C for 3 hours. The cooled blocks were then affixed to a tensile tester (Testometric 350, Rochdale). An extension rate of 10mm min^{-1} was used for the tensile testing.

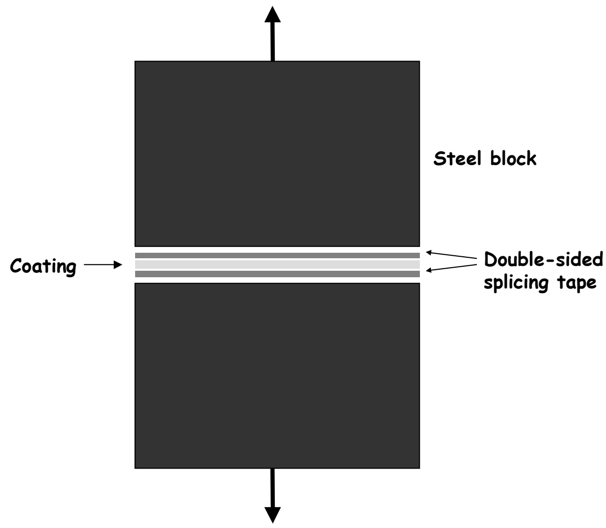


Figure 1. z-directional tensile block assembly

The measurement of z-direction tensile strength required some development. Simply attaching the coating and metal block assembly with adhesive tape prepared using pressure alone resulted in failure of the tape – coating interface. A solution to this was developed in which the coating / adhesive tape / block assembly was heated in an oven at 90°C for a minimum of 3 hours. After this, the tape was capable of holding the coating to the steel surface, and the failure occurred within the coating.

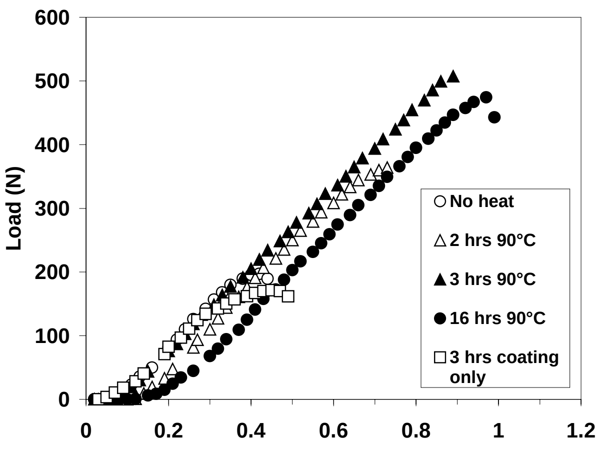


Figure 2. Conditions for z-directional tensile, Clay A + 5 pph latex

Figure 2 shows the output from the tensile test using a latex level of 5 wt% for various times at 90°C. Heating the coating layer to 90°C before attaching the tape gave the same result as the unheated assembly, showing that the heat treatment was affecting the adhesion of the tape to the metal and coating surfaces, not the binding ability of the latex film. More evidence for this conclusion was also gained by heating some coatings at 90°C for 3 hours before cutting into barbell shapes and measuring the in-plane tensile strength. The in-plane strength was the same for heated and unheated samples.

Above a certain latex level, adhesion failure was observed between the tape and steel block. The level at which this occurred was the same as observed for a blank experiment using just tape between the steel blocks (**Fig 3**). Above this latex level, it is assumed that failure occurs between the tape and blocks or within the adhesive rather than within the coating layer. Hence measurement of z-directional strength has so far been limited to latex levels below about 10 wt%. However, the linear nature of the tensile strength development allows extrapolation to higher latex levels.

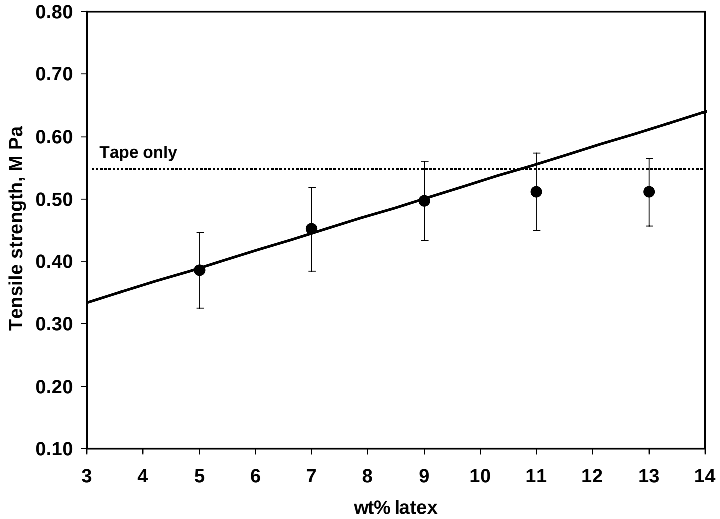


Figure 3. Z-directional tensile strength as a function of latex level for films of kaolin D.

In both types of test the result was calculated by dividing the load (N) at break by the cross-sectional area to give the tensile strength in MPa. The elongation obtained with applied load was also recorded. **Figure 4** compares results for the same coating in the two different directions. The elongation axis is expressed as strain, i.e. as a fractional increase in length.

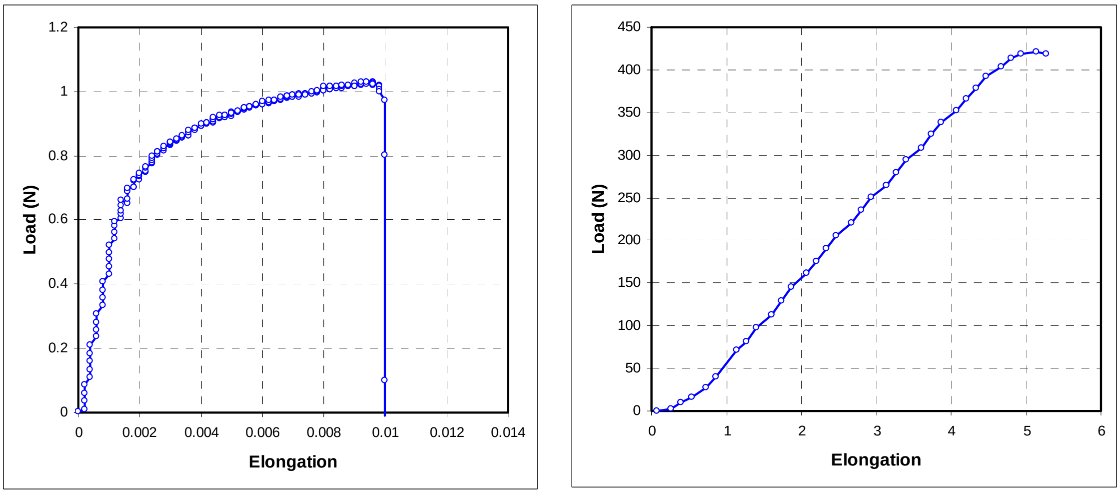


Figure 4. Comparison of load / elongation curves for coating (Clay A / 5pph latex) in the in-plane (left) and z- (right) directions. The different loads applied relate to the relative cross sectional areas used for each test.

We observed that the elongation in the z-direction test is very much larger than in the in-plane test. The order of extension is so great (ca. 500%) that it suggests some kind of artefact. A test with just tape between the steel blocks showed similar levels of extension. We think that the tape and adhesive layers must be capable of elastic elongation, whilst still acting to deliver the stress. The different shapes of the curves were due to the different elongation rate, since a constant strain rate was applied. Hence with this technique it is not possible at present to study elongation or Young's modulus in the z-direction.

Effect of Coating Layer Thickness

To explore the effect of thickness, coatings using the same formulation were prepared at different coatweights using different wirewound bars. A range of thickness values from around 50 to 150 µm were produced. For the results reported in the next sections, we used a coating thickness range between 50 and 100 µm.

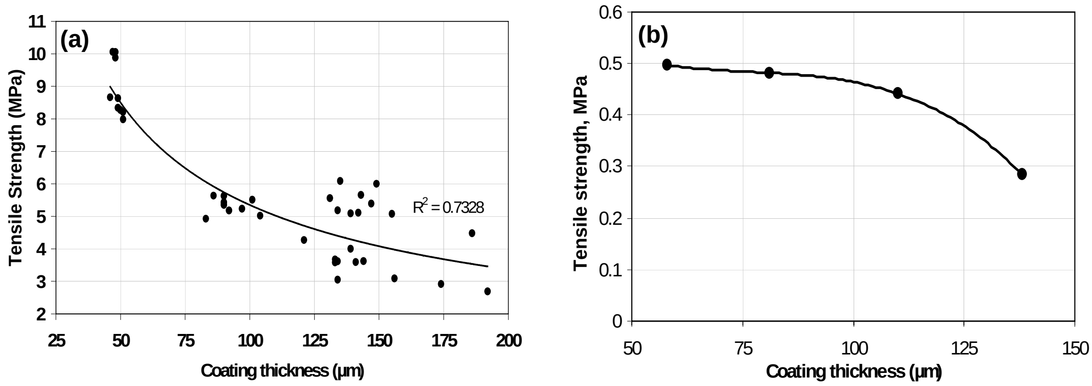
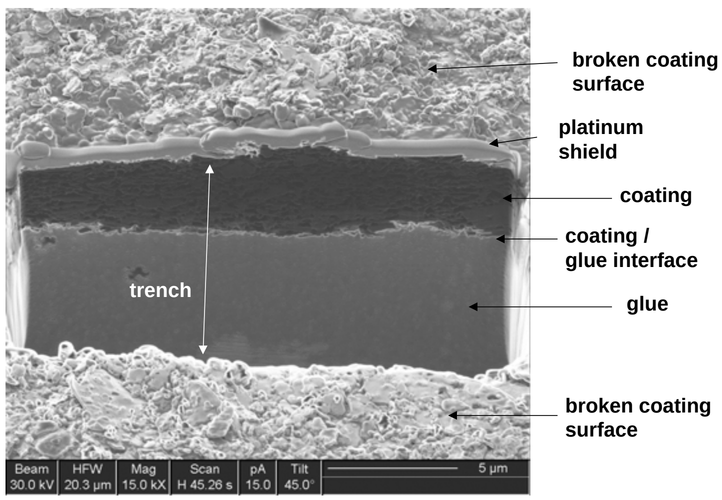


Fig 5. Effect of coating layer thickness on (a) in-plane and (b) z-direction tensile strength of coatings based on clay D with 9 pph latex.

Figure 5(b) reveals that the tensile strength in z-direction falls as coat weight increases. This suggests that in thicker coatings, the mechanics of the coating versus tape behaviour swings toward dominance by the coating, and it may well be that the deformation of the tape prevents accurate stress transmission until coat weight is higher. The tape may apply lateral (x-y) stress to the coating layer by the action of the lateral deformation even under z extension, i.e. when the coating is thin, such that the true z direction strength is only revealed at high coat weight. Due to uneveness in the coating – tape interaface, there are lateral components of stress due to the deformable nature of the tape. As coating thickness increases, these lateral stresses decrease in proportion to the z direction component stress in the thick coating. Since the lateral stresses for clay can be tolerated better than the z directional, so the strength of a thin layer may appear stronger.

Penetration of Adhesive

When using uncoated papers, penetration of adhesive into the sheet is known to affect the measured strength values by reinforcing the outer layers of the sheet [7, 9]. In order to establish if this phenomenon occurred in the coating layer, a Focussed Ion Beam (FIB) spectroscopy method was used to image the tape – coating interface. The technique has been used in previous studies to image the penetration of organic ink components into paper coatings [12, 13]. A coating based on kaolin D and ground calcium carbonate (GCC) and 5 pph latex was used. Such a combination will give a coating layer of high porosity which will be most likely to absorb adhesive. The coating layer was imaged after subjecting it to the z-direction tensile test. A FEI FIB201 ion beam instrument was used for sectioning and high resolution imaging. The instrument produces a gallium ion beam of between 7 and 300 nm in diameter at 30 keV. A platinum organometallic gas injector allows ion beam assisted deposition of platinum over selected areas of the sample. This was carried out prior to sectioning in order to protect the top surface of the sample during ion milling. For sectioning the sample, a high ion current was used initially to remove a staircase – shaped trench. A finer beam of lower current was then used to polish the vertical face of the trench . The sample was then tilted to 45° and the polished face imaged using the same beam at a lower current to achieve high resolution. The technique showed the broken surface of a coating layer (coated with Pt) and revealed the interface with the tape adhesive. Typical cross sections are shown in **Fig. 6**. The organic adhesive layer is visible at the bottom of the image. The higher brightness of the adhesive layer compared to the mineral particles above it is due to its higher conductivity, which keeps the potential of this region of the sample low. The mineral particles have a higher electrical resistance which results in a much higher potential, which curtails the emission of secondary electrons, making them appear darker. The interface of the adhesive with the coating surface shows up as a bright line. These images clearly demonstrate that penetration of adhesive beyond the surface roughness features of the coating layer has not occurred. Given that the coating pores are between 0.1 – 0.15 μm in diameter, penetration of a viscous adhesive would be unlikely to occur.



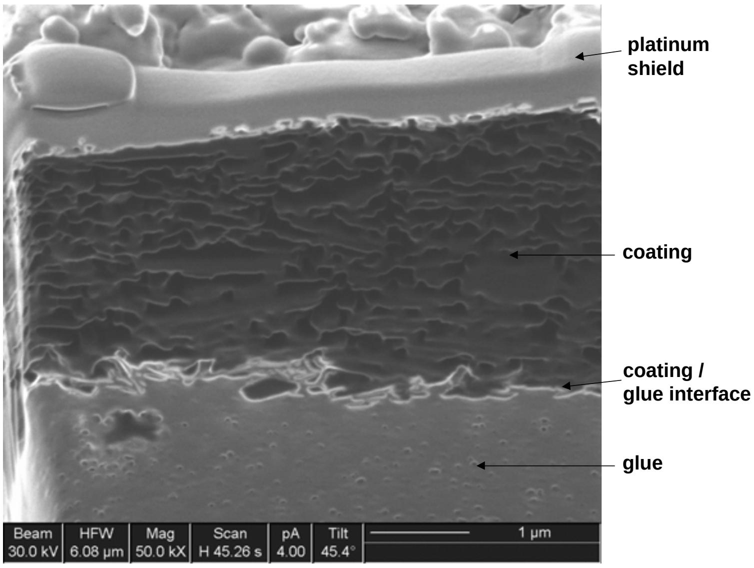


Figure 6. Section showing coating / adhesive interface imaged using focussed ion beam. Above : section of coating surface and ion-milled trench, below : view of coating – adhesive interface showing no penetration of adhesive beyond the coating surface. Coating based on 55: 45 kaolin D: GCC blend with 5 pph latex.

RESULTS

The Effect of Binder Level on Tensile Strength

Figure 7 shows a typical set of results for coatings made from single clay (B) at different latex levels. Both tests show that strength increases with binder level, but the z-direction strength is substantially lower than the in-plane strength. **Figures 8** and **9** summarise the results for all the clays in the in-plane (**Fig 8**) and z direction (**Fig 9**). As latex levels are increased, both in-plane and z-direction strength increases linearly for all 4 clays tested. It is clear that all the coatings are much weaker in the z-direction than in-plane.

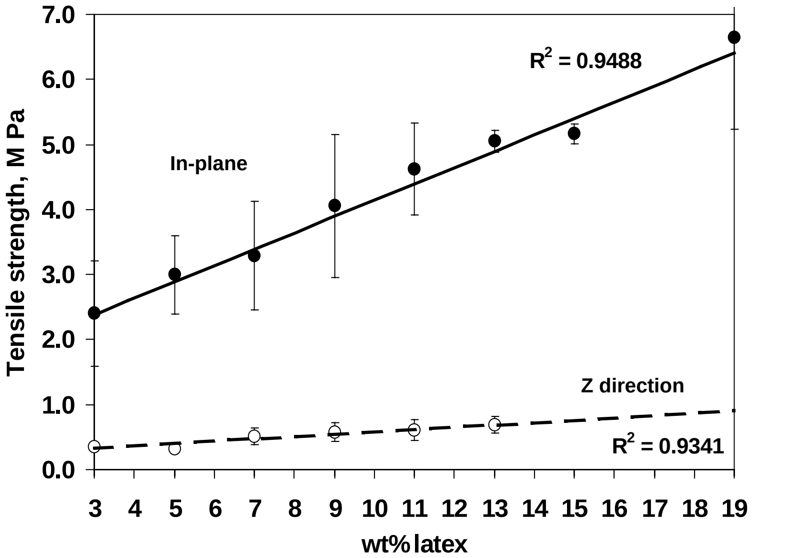


Figure 7. In-plane and tensile strength of coatings based on kaolin B at a range of latex levels.

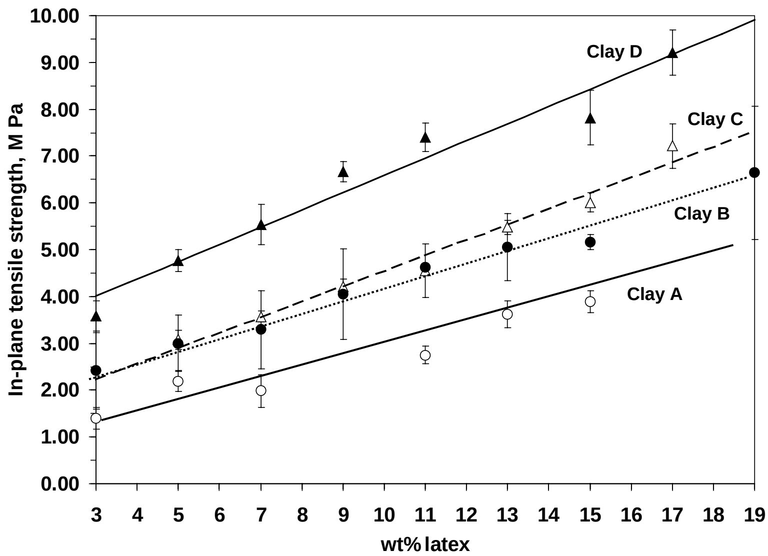


Figure 8. In-plane tensile strength as a function of latex level, all clays.

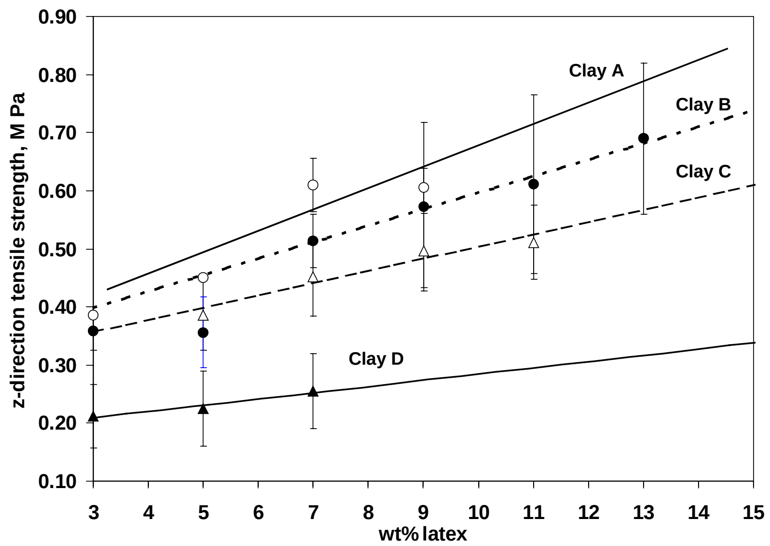


Figure 9. Z-direction tensile strength for the coating films in Fig 8.

Figure 10 shows the ratio of in-plane to z-direction strength for these clays across the range of latex levels. These ratios were calculated from **Figs 8** and **9** using the best fit lines. Values range from 4:1 for the low shape kaolin to 22:1 for the finest platey clay.

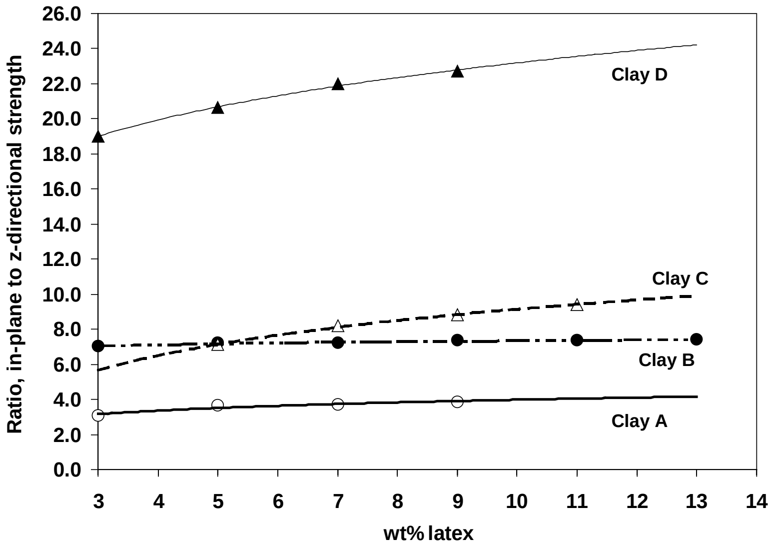


Figure 10. Ratio between in-plane and z-direction tensile strength for coatings in Figs 8 and 9.

Plotting the in-plane strength as a function of z-direction strength for a single latex level (12 wt%) shows an inverse linear correlation (**Fig. 11**). This means that as the in-plane strength increases, the z-direction strength is reduced.

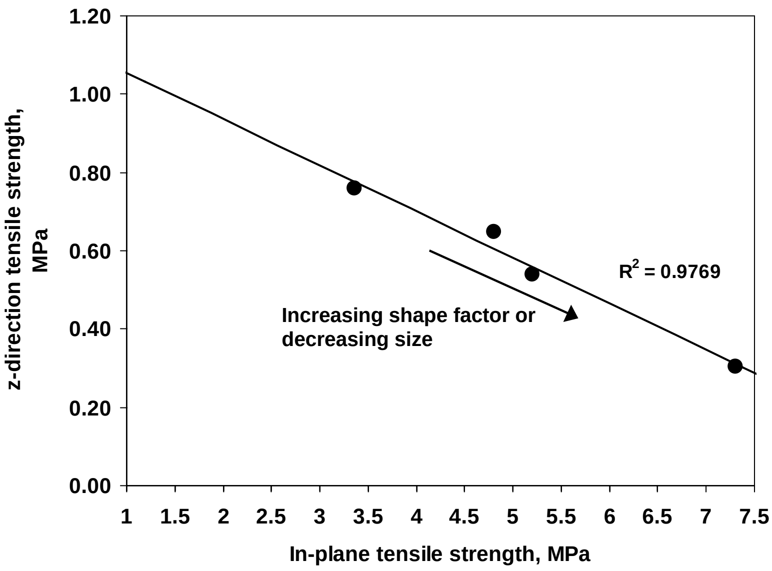


Figure 11. z-direction vs. in-plane tensile strength for coatings containing 12 wt% latex. Data interpolated from Figs 8 and 9.

Comparison with Calcium Carbonate

Measurement of the strength of coating films containing 100 parts of GCC (90wt% < 1μm) proved to be difficult because the films are very fragile in the in-plane direction, and too strong to measure in the z-direction. Blends of GCC with different levels of clay D were made at a latex level of 5 pph, and tensile strength measured on these. The in-plane and z-direction strength of 100% GCC films were then estimated by extrapolation (**Fig. 12**). The extrapolated values for in-plane and z-direction strength were in good agreement, indicating an absence of anisotropy in GCC coating layers.

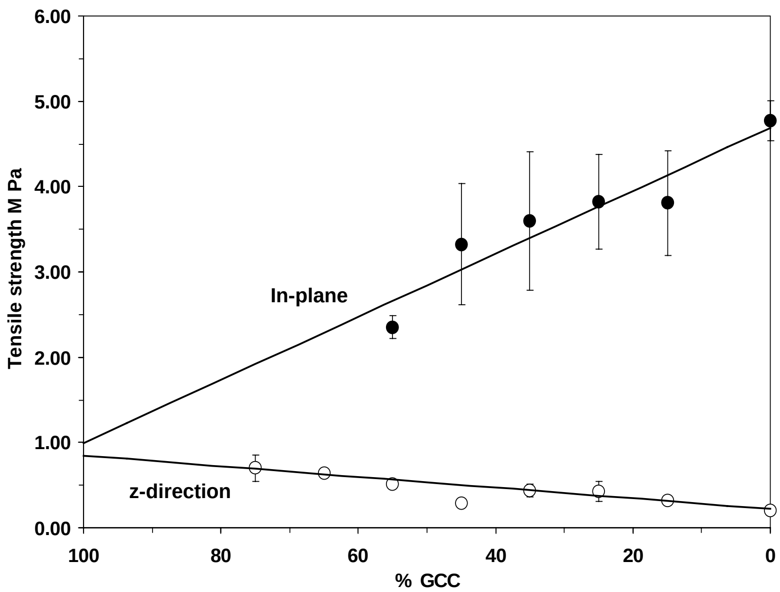


Figure 12. In-plane and z-direction tensile strength measured on blends of GCC (90wt% < 1μm) and clay D at a latex level of 5 wt%.

DISCUSSION

This work has shown that the morphology of kaolin has a major effect on the strength of the coating layer. By developing a method to measure the tensile strength of the coating in the z-direction using the same principle as the in-plane test, we were able to show that coatings based on platey kaolin are weaker in the z- than the in-plane (x-y) direction. This agrees with previous studies using a rolling cylinder method [3] and using a microindentor [5]. Increasing the aspect ratio of the kaolin particles led to higher in-plane tensile strength and lower z-directional tensile strength. The same trend was observed when the mean particle size of the clay was reduced from 0.4 to 0.2 µm. The inverse relationship between strength parameters measured in different directions reflects the anisotropic nature of the clay particles and shows that the properties affecting the coating strength are different depending on the direction in which the stress is applied.

These results show some interesting parallels with the strength properties of uncoated papers. Baum et al. [14] showed that the z-direction tensile strength is two orders of magnitude less than in the plane of the sheet. This is attributed to the in-plane strength being influenced by the strength of the fibres themselves and the z-direction strength by the interfibre bonding. That such a mechanism applies to a coating is open to question given the much smaller disc diameter of pigment particles compared to the length of fibres.

Coating layers based on blocky ground calcium carbonate particles gave weaker in-plane tensile strength than clay, but higher z-directional strength. Values for the in-plane and z-direction strength were the same for GCC layers. This suggests that isotropic coating structures are formed using GCC, as would be expected. The results also suggest that for equal in-plane tensile strength, GCC layers are stronger in the z-direction than clay layers. This might indicate that the adhesion of latex is stronger to basic calcium carbonate surfaces than acidic clay surfaces, as suggested by Granier and Sartre [6], although it could be argued that polyacrylate dispersant molecules already occupy these basic sites. Parpillon suggested [15] that the latex is more evenly distributed on $CaCO_3$ than kaolin, where they postulated that latex is localised at particle edges. Some evidence for this is found in a scanning electron microscope study by Krugge et al. [16]. Another mechanism suggests that the mode of deformation of the latex interparticle bridges may be different in different directions. In-plane deformation of layers of aligned plates will subject the latex to shearing, whereas applying stress in the z-direction should subject the latex to elongational deformation. In isotropic GCC layers, there will be equal distribution of shear and elongation with direction.

In practice, the strength of coating layers during calendering and printing depends on the relative component of in and out of plane deformation during the process, as well as the extent of interaction or tack development between the ink and coating during the test. In the case of wet pick, the rate of absorption of the water film by the coating will affect the result. It is possible that the z-direction strength measurement could be modified to measure wet strength, although a different tape with an insoluble adhesive would be required. It is our next aim to correlate the trends reported above with the printing strength properties of coated papers containing the same pigments.

CONCLUSIONS

This work has shown that :

a) Coating layers based on kaolin particles possess anisotropic strength properties. Depending on the particle size and shape factor, the in-plane tensile strength of the layer is greater than the z-direction strength by factors of between 4 (in the case of coarse and blocky particles) and 22 (using fine and platy particles).
b) When a series of coatings based on kaolins of varying size and shape were compared, there was an inverse relationship between in-plane and z-direction strength. High shape factor particles gave coating layers having the highest in-plane but lowest z-direction strength.
c) Coatings based on blocky GCC particles showed similar z-direction and in-plane strength, confirming that this pigment gives isotropic coating structures.
d) High latex levels using coatings based on the same clay type increase both strength parameters.

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Authors' statement

We chose to study the strength properties of coating layers because, surprisingly, there is relatively little recently-published work in the open literature. Shape-engineered kaolins have recently entered the market and we were interested to see if there were any advantages such pigments could offer in conferring stiffness or resistance to cracking, for example. In the current economic climate, the move to lower basis weights and the need to optimise binder use are important and the availability of a further control tool such as kaolin morphology is a valuable asset for the papermaker.

The biggest challenge we encountered in this work lay in the development of the practical technique for measuring the z-direction tensile strength of coating layers which are only 100 µm thick. The use of double-sided tape was at first unsuccessful until we tried heating the tape / coating assembly in the oven to anneal the interface. We used a splicing tape manufactured for splicing reels of coated paper, which we happened to have a supply of in our lab. We then had to prove that the glue from the tape was not penetrating into the coating which we did using the Focussed Ion Beam imaging facilities at the University of Bristol.

There have been previous attempts to measure z-direction strength of paper coatings but these have used a different technique to that used in the xy direction. We believe that our work is the first to obtain measurements of the anisotropy in tensile strength using comparable methods and correlate the results with the shape factor of the particles.

We are currently carrying out further studies which are aimed at relating the strength properties measured on unsupported films to the pick properties of papers coated with the same pigments.

IMERYS
Pigments for Paper

Europe
Tel: +44 1726 818000

Asia Pacific
Tel: +65 67 99 60 60

N. America
Tel: +1 770 594 0660

S. America
Tel: +55 11 2133 0055

Email
paper@imerys.com