

The influence of pigment particle shape on the in-plane tensile strength properties of kaolin-based coating layers

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ABSTRACT: The mechanical properties of paper coating layers are critical to converting and printing operations. These include stiffness, resistance to fold cracking, dusting, and pick resistance. For this study, we prepared unsupported coating layers and measured the in-plane tensile strength as a function of the kaolin particle shape factor. We found that, for kaolin pigments having a similar particle size by sedimentation, in-plane tensile strength and stiffness of the coating layer increases as the shape factor of the clay particles increases. Conversely, elongation to break decreases. These observations are interpreted in terms of the microstructure of the coating layers. A second observation is that elongation increases exponentially with latex level. This suggests that at latex levels normally used in paper coating, the polymer chains are constrained by adhesion onto pigment surfaces and are less extensible than in the bulk latex film.

Application: 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.

Among the mechanical properties of coated papers, stiffness and strength are perhaps the most important. As basis weights decrease, maintaining the stiffness of coated papers is desirable. The surface strength of coated paper is critical to the printing process. Resistance to cracking is important during the converting of paper and board.

When paper strength problems occur, understanding the cause can be complicated. Several strength parameters are important, reflecting the handling, converting, and end use of the paper. For example, dusting at the calender is an indication of inadequate surface strength, as is picking during printing. However, pick may occur in the litho area (wet pick) or in the dry area, where it may cause dusting. The mechanisms of each will clearly differ. Pick within the coating layer itself is different from rupture at the coating-base-stock interface. Wet rub resistance is also required in certain applications. Here the presence of soluble binder might be influential. During the converting process,

cracking at the fold may indicate inadequate coating tensile strength.

In any coating application, the first prerequisite to obtain adequate strength is that there is sufficient binder present. This raises the issue of the “binder demand” of the pigment, but there are still some uncertainties about which pigment properties are most important in its determination. Many researchers believe that surface area is most important, although Cobb [1] was unable to show this. Dating back more than 50 years, her work clearly established a correlation of binder (casein) demand with the pore volume of the pigment in a coating layer. This is not unexpected; porosity in a material reduces its strength because the voids have no load-bearing ability. Using this argument, pigments that increase the porosity of the coating should require more binder. However, such pigment designs may lose binder more readily into the base paper, which might weaken the coating strength, but paradoxically may strengthen the coating-base sheet interface.

Since Cobb’s paper, there have been

surprisingly few published studies on coating strength. Parpillon et al. [2] measured the tensile strength of coating layers of 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 elongation at rupture. These trends correlated with stiffness. The study also showed, not surprisingly, that both tensile strength and elongation to break increased as the level of latex increased. Similar trends were observed as the T_g of the latex was decreased (i.e. as the latex became softer). Dynamic mechanical and nuclear magnetic resonance (NMR) experiments on the films suggested that the binder existed in discrete domains in the clay films, but was spread more evenly over the GCC particles.

This explanation was also supported by the work of Lepoutre and Hiraharu [3] who investigated the differences in mechanical properties of coating layers of calcium carbonate and kaolin, this time in the z-direction. Using the IGT pick test with oil, they concluded that

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the mechanical strength of the GCC coatings was higher than that of the clay. Using a rolling cylinder technique to measure z-directional strength, they found that the rupture energy of the GCC layer was higher than that of 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 [4].

Subsequently, Lepoutre and Rigdahl [5] examined a wider range of pigments of different shape and related the in-plane elastic modulus of coating layers to the presence of voids. Hence, in blends with clay, isometric GCC particles reduced the elastic modulus more than needle-shaped aragonite at the same adhesive level. Further studies of the z-directional strength of kaolin and GCC layers were reported by Inoue and Lepoutre [6]. 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 (CMC). Coatings of monosized polystyrene pigment had the lowest peel energy. The critical binder content was determined from the peel test and correlated with pigment surface area. They concluded that coating layers based on plate-shaped clay particles, in comparison with isometric GCC, were more resistant to in-plane stresses.

Recently, work has been published on z-directional coating strength of paper using a micro-indentor [7]. 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. Granier and Sartre [8] provided an alternative view. They interpreted the strength of coatings in terms of the acid-base character of the mineral and latex. 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. Also, styrene-butadiene latex should adhere more strongly to basic calcium carbonate than to kaolin, but this does not support the published in-plane tensile strength trends. Nonetheless, the effect of surface chemistry on binder-mineral adhesion should form part of any comprehensive theory of coating strength.

Our present study focuses on the role of kaolin particle shape in determining the mechanical properties of coating layers, particularly the in-plane tensile strength. Engineering the particle shape factor, or aspect ratio, has

made kaolin a very versatile coating pigment that confers additional functionality to coating formulations [9, 10].

MATERIALS & METHODS

Materials

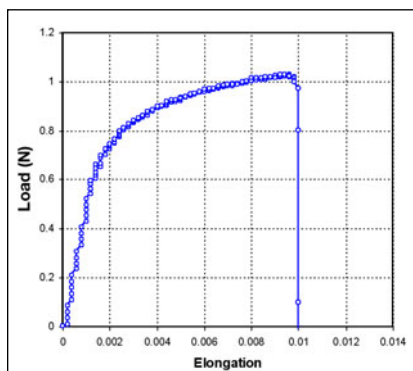
We used a series of three coating kaolins having approximately similar particle size distributions as determined by sedimentation. These were chosen to cover a range of particle shape factor values, from blocky to very platy. The mean (D50) particle size was 0.40 μm equivalent spherical diameter (esd). Additionally, two ultrafine kaolins were included of blocky and platy morphology. These had a mean size of 0.20 μm . A GCC of 90 wt% <2 μm (Carbital 90™, D50 = 0.60 μm) was also used in some experiments.

Table I summarizes the properties of the kaolins. The mean shape factor (defined as the average plate diameter/thickness) was measured by stopped flow conductivity using a patented technique [11]. The shape factor 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 $T_g = 10^\circ\text{C}$ (DL920, Dow Chemical).

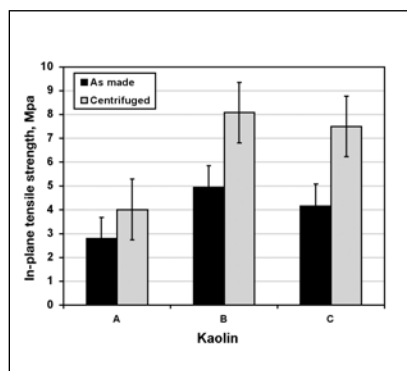
The kaolins were slurried at the optimum solids using 0.3 wt% of a sodium polyacrylate dispersant (CED3546, Ondo Nalco). The latex was added at levels between 3 and 17 part per hun-

KAOLIN	TYPE	PARTICLE SIZE DISTRIBUTION BY SEDIGRAPH, wt% BELOW					D50 BY LIGHT SCATTERING (MALVERN) μm	SHAPE FACTOR	BET SURFACE AREA, m^2g^{-1}
		2 μm	1 μm	0.5 μm	0.25 μm	D50 μm			
A	Secondary	93	81	63	34	0.37	1.46	16	14
B	Primary	90	74	55	31	0.44	1.52	34	16
C	Secondary	90	77	60	34	0.40	3.1	56	16
D	Secondary	100	99	94	68	0.19	0.32	10	27
E	Secondary	97	90	79	53	0.23	1.43	40	24

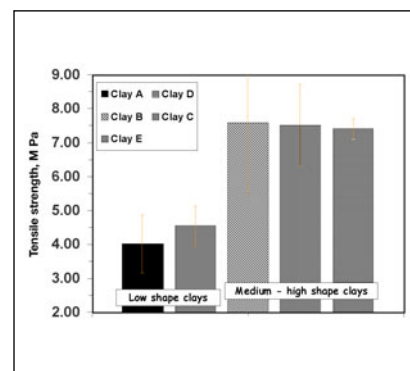
I. Physical properties of kaolins.



1. Example of a load; elongation curves for coating (clay A, 5 pph latex) in the in-plane direction.



2. Tensile strength of coating films prepared with and without centrifuging to remove air.



3. Tensile strength of coating layers containing 12 wt% latex and 0.3 wt% CMC.

dred (pph), based on clay. We also added 0.3 pph of sodium carboxymethyl cellulose (Finnfix 10™, Noviant) as a thickener. After pH adjustment to 8.0, the colors were screened through 53 μm .

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.), which had a caliper of 13 μm . Prall [12] found that this gave 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 wire-wound bar (Sheen Instruments, Kingston, UK). Typically, 100 μm thick films were produced. Following drawdown and drying with a hot air stream, we found that most pigment binder combinations could be easily separated from the substrate and were sufficiently self-supporting to handle. The exceptions were in 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 50 mm, and the width of the central bar was 4 mm. The thickness of the film was measured using a caliper gauge (Messmer), accurate to $\pm 2 \mu\text{m}$. 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.

Figure 1 shows an example of the output. 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). Five measurements were made on each sample, and the mean value calculated. In the following figures, error bars signify the standard deviation.

We improved our results by removing air bubbles from the coatings. We did this by centrifuging the colors at 4000 rpm for 10 min. **Figure 2** shows the improvement in in-plane tensile strength obtained after removal of air by this method.

The specific surface area of coating films was measured by nitrogen adsorption using a 3-point Brunauer-Emmett-Teller (BET) method with a Micromeritics apparatus. Samples were out-gassed at a temperature of 100°C. The pore size and volume of coating layers were measured by mercury intrusion using a CE Instruments Pascal 240 porosimeter. Corrections for glassware expansion were applied.

RESULTS

The role of particle shape on tensile strength

Our first experiments compared the in-

plane tensile strength of unsupported coating layers based on clays A-E at the same latex level, 12 wt%. Results (**Fig. 3**) demonstrated that higher shape factor kaolins gave stronger coatings in this direction.

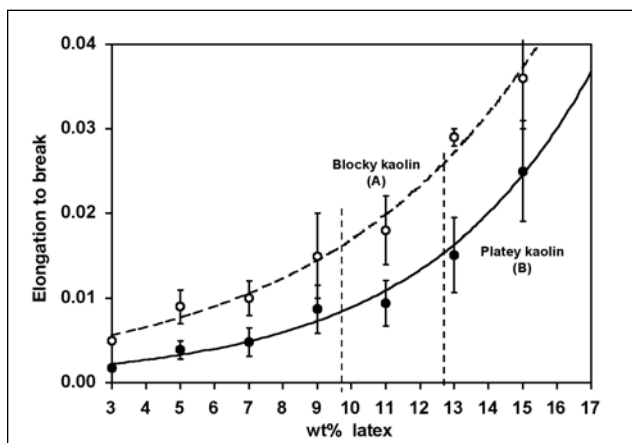
This advantage in tensile strength from higher shape factor clay was also found when blended with blocky GCC of 90 wt% <2 μm esd (**Fig. 4**). To measure the very fragile 100% carbonate coatings, we modified the tensile test method to reduce the rate of extension to <1 mm min⁻¹.

When platy clay E was substituted for blocky clay D at 20 parts the improvement in tensile strength was about 1.3 MPa, which is the same as that obtained by increasing the latex level by 4–5 parts (**Fig. 5**).

The effect of binder level on tensile strength

Two sets of coatings were prepared based on clays A and B. Latex level was increased from 3 pph to 15 wt%, keeping the CMC level constant. A third set of coatings was prepared using GCC of 90 wt%, <2 μm , containing 20 parts of clay E. **Figure 5** shows that the in-plane tensile strength of the coatings increased linearly with the latex level. All of the pigments gave, within acceptable error, a similar slope. The advantage of the platy clay in conferring in-plane strength is also clear from this graph.

Plotting the effect of latex level on specific surface area for the two clay coat-



8. Elongation to break as a function of latex level for coatings with clay A (blocky) and clay B (platy).

which has elongation properties closer to the bulk polymer. The surface area trends shown in Fig. 6 offer some support for this theory. The reduction in surface area probably indicates the presence of regions of coherent latex film between kaolin particles.

The role of kaolin particle shape on mechanical properties

Kan [17] showed that the stiffness of the coating layer can be correlated directly with the elastic modulus of the coating layer. Measurement of the stiffness of coated papers showed that using higher shape factor kaolin enables stiffness to be increased. **Figure 9** shows the results of coatings on 62 gm⁻² medium weight coated (MWC) mechanical base paper using clays A and C in a formulation containing 11 wt% latex and 0.3 wt% CMC. The coatings were applied using a cylindrical laboratory coater (Heli-Coater™) and the stiffness of the calendered strips measured using a Kodak Rigidimeter™. This instrument measures the free sample length of a paper strip 15 mm wide vibrating at 25 Hz at maximum amplitude. The scatter in these measurements is large, reflecting the rather low and variable stiffness of lightweight coated papers.

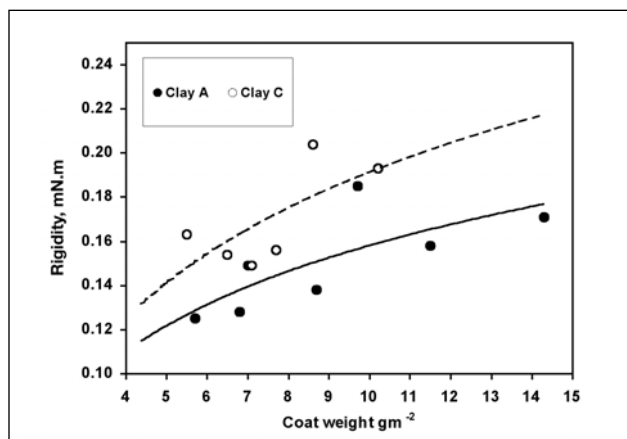
The high shape factor clay C increased the stiffness of the coated paper by around 20% compared to the low shape factor clay A. This correlation with in-plane tensile strength is to be expected

because the coating will be either in tension or compression during bending.

DISCUSSION

This study shows that the morphology of kaolin has a major effect on the mechanical properties of the coating layer. For clays of similar particle size distribution by sedimentation, the in-plane tensile strength increased with the shape factor of the kaolin. These trends correlated with the stiffness of coated papers made with the same clays. We may also expect to see benefits in resistance to cracking during folding, which has been related to tensile strength [18].

In-plane tensile strength of coating films increased and surface area of the coating fell as the latex level increased. In the limit, at very high latex levels, pores will be filled and the system will effectively become a film of latex polymer containing filler and the surface area will be close to zero. Measuring the elongation to break as a function of latex level revealed that, above a critical binder level, the coatings became more extensible. The critical binder level was around 11–12 wt% latex for the particular pigments used here, which is the same as the level commonly used in offset coating formulations. We postulate that below this level of latex, polymer molecules are constrained by the pigment surfaces, as a result of adhesion. This reduces their mobility. Above the critical binder level, surface coverage increases and unconstrained latex be-



9. Stiffness of coated papers (clays A and C) showing effect of shape factor.

comes available, which is similar to bulk polymer and more able to undergoing elongation. We suggest that this method could be used to compare binder demand for different pigments in isolation from the base paper.

In summary, these trends are parallel to those seen in mineral-filled polymer systems. Increased filler platiness and reduced particle size increase stiffness in filled polymer systems [19, 20]. This is interpreted as arising from an increased number or area of basal surfaces, which can dissipate energy as they slide over each other, in a similar way as we observe increases in suspension viscosity, for example. However, the presence of air-filled pores in our case will provide weak-link locations where failure may occur under stress. The reduced elongation to break found with platy kaolins correlates with the reduced impact strength they give in filled polymers. This may arise from stress concentration along particle or pore edges, which are longer in the case of high aspect ratio particles [19, 20].

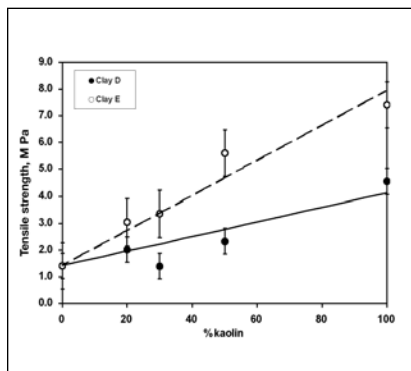
The effect of pigment morphology on z-directional strength is of equal interest and is the subject of further research.

CONCLUSIONS

This work has shown the following:

1. The in-plane tensile strength of a kaolin-based coating layer is influenced by the shape of the particles. Using high shape factor kaolins enables the

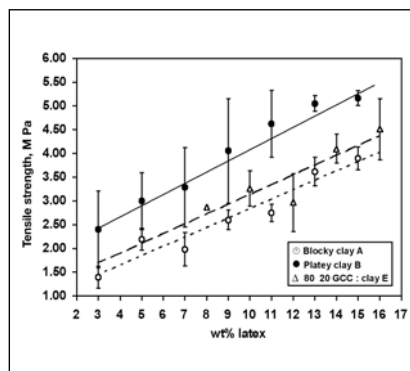
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4. Tensile strength coatings based on blends of kaolin D and E with ground calcium carbonate and 12 wt% latex / 0.3 wt% CMC.

ings showed that surface area decreased as latex level increased, reaching a limiting value at higher latex levels (Fig. 6a). At very high latex levels below the critical pigment volume concentration (CPVC), the surface area will approach zero as all the pores become filled with binder. The reduction in pore volume as latex level increases follows a similar trend to the reduction in surface area (Fig. 6b). There was no discernible effect of shape factor on the pore volume.

When surface area was plotted against the in-plane tensile strength (Fig. 7) results for the two clays still fell on separate curves, showing that differences in surface area alone were



5. In-plane tensile strength as a function of latex level, kaolin A (blocky), kaolin B (platey), and an 80:20 ground calcium carbonate (GCC):kaolin E blend.

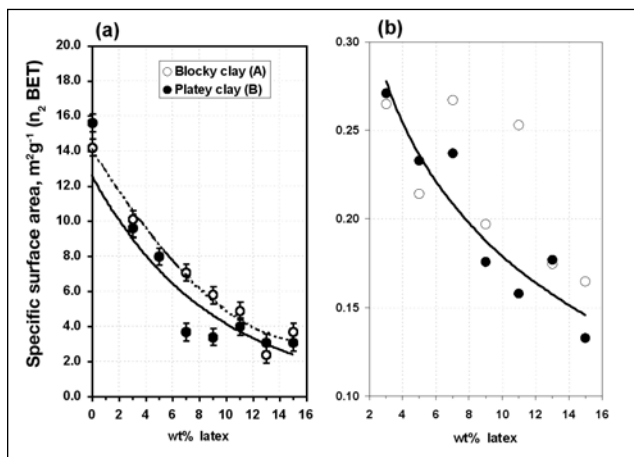
not responsible for the higher strength of the platy clay coatings.

The elongation behavior (Fig. 8) showed that elongation to fracture increased exponentially with binder level.

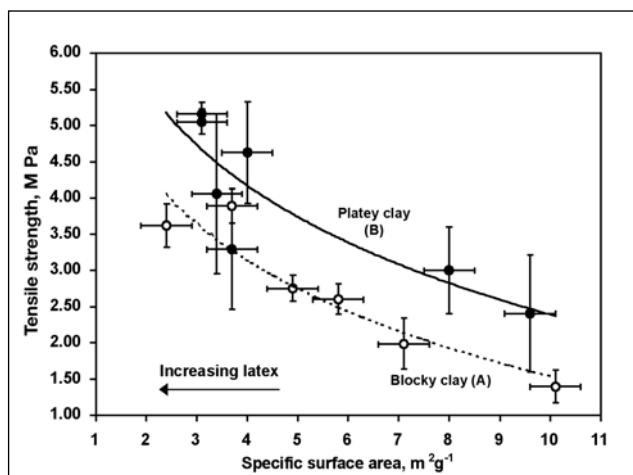
A critical binder range over which elongation begins to increase faster is seen between 10 wt% and 13 wt% binder. Transition points often occur when film properties, such as porosity, gloss, or drying stress, are plotted against binder level. In these cases the discontinuity indicates the CPVC of the system (i.e., the point at which all voids are just filled with binder). However, CPVC values of typical coating formulations con-

taining kaolin and GCC occur at latex levels of around 30 wt% [13], much higher than we have used here. Therefore, the elongation behavior seen in Fig. 8 cannot be related to the system CPVC. The pore volume data in Fig. 6(b) confirm this conclusion. It may be significant that the critical region occurs at binder levels typical of those used in offset papers.

We suggest that, below this critical range, most of the latex may be spatially bound to the available pigment surface, and therefore this constrained binder film is less able to undergo extensive elongation. The literature presents evidence for an interphase region around filler particles in polymer matrices [14, 15]. Parpillon et al. [2] demonstrated that latex associated with pigment in a coating film has a higher T_g than the pure latex film, indicating that the chains have restricted mobility. This conclusion was confirmed by Hagen et al [16], who measured the shift in T_g as a function of the clay-to-latex ratio. When the clay was a minor component of the coating, the T_g of the latex was similar to the bulk polymer. At low levels of latex typical of paper coatings, the T_g was about 5°C higher, indicating less polymer mobility. We can interpret the greater elongation above 11 wt% as evidence that at these higher binder levels, more unconstrained polymer is present,



6. (a) Specific surface area (N_2 BET) and (b) pore volume (mercury intrusion) of coatings based on blocky and platy clay. Coatings were outgassed at 100°C for surface area.



7. In-plane tensile strength of clay A and B coatings plotted as a function of surface area.

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in-plane strength to be increased compared to blocky particles of similar equivalent spherical diameter. This will result in benefits in stiffness and, probably, folding resistance [18].

2. Adding only 20 parts of high shape factor ultrafine kaolin to a ground calcium carbonate allowed significant increases in tensile strength to be obtained compared to an equivalent low shape factor glossing clay. In this instance, the increase was the same as that obtained with an additional 4–5 wt% latex.

3. The elongation behavior observed in the tensile test depends on the binder level. Above a certain binder range, greater elongation is seen, which we believe indicates the appearance of regions of unconstrained binder as opposed to polymer constrained by adhesion to the kaolin. This may be a way of determining the optimum latex level for a pigment independently of base paper interactions.

Application studies are planned to determine whether the increased in-plane strength of these shape engineered kaolins will increase the resistance of the coating to cracking at the fold, for example. TJ

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INSIGHTS FROM THE AUTHORS

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 optimize binder use are important. The availability of a further control tool such as kaolin morphology is a valuable asset for the papermaker.

The biggest challenges we encountered in this work lay in the development of the practical techniques for preparing unsupported

coating layers and removing them from the substrate. We found a good substrate was thin polyethylene terephthalate film, obtained from a local cookstore and normally used for roasting meat.

We are carrying out further studies, which are aimed at relating the strength properties measured on unsupported films to the strength properties of papers coated with the same pigment-binder combinations.



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