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Analysis of the effect of porosity and pigment shape on the stiffness of coating layers

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The elastic modulus of paper coating layers made of mineral pigments and containing 9% by weight of a synthetic binder was measured at 23° C. The mineral pigments used comprised clay, ground natural calcium carbonate and different forms of precipitated $CaCO_3$ (aragonite, rhombic and scalenohedral). The pigments used differed in shape from isometric to plate-like and needle-like particles. From the measured values of the modulus, the corresponding values of void-free coatings were evaluated using a model proposed by Bert which also accounts for the effect of stress concentrations due to the presence of the voids. The calculated modulus values of the void-free coatings were compared with predictions from composite theory, e.g. the Halpin–Tsai equations. In general, a reasonable agreement was noted indicating that paper coatings of this type can be regarded as composite materials and can be analysed with the methods used within that field.

1. Introduction

An effective way of improving the optical properties and the printability of paper and board is to apply a thin coating layer, 3 to 10 μm thick, consisting mainly of mineral pigments, with a small amount of binder. The corresponding coat weight on the substrate may be in the range 5 to 15 $g\,m^{-2}$. The coating is applied as an aqueous suspension and then dried. The mechanical properties of the coating layer and its adhesion to the base paper are of concern in many situations. The coating must be sufficiently strong and ductile and adhere sufficiently well to the base paper to sustain without rupture the loads exerted on it during converting and printing. The resistance of coated paper during printing has thus been studied rather extensively, see e.g. [1, 2], but few investigators have examined the strength characteristics of the coating layer [3, 4].

The elastic modulus of the coating layer is also of importance. Because its magnitude is comparable to that of paper and the coating layers are located far from the neutral plane, it is expected that they can influence the bending stiffness of the coated paper. A high bending stiffness of the paper product is desired especially in applications such as sheet printing and reprography or for paperboard in connection with packaging applications. In this connection it is of interest to know how the elastic modulus of the coating layer is affected by the mineral pigments and the structure of the layer. This is dealt with to some extent in this article.

A paper coating can be considered as a composite material consisting of mineral pigments, binder and air. The air voids, which result from a low binder content, account for the light scattering of the coating. They may amount to 15 to 40% of the coating volume depending on the type of pigments and on the binder level. This porosity will have a strong influence on the modulus of the coating layer and an attempt is made here to incorporate its effect using composite theories. The elastic modulus of the binder and the shape and modulus of the mineral pigment are also expected to affect the elastic properties of the coating.

In order to obtain coating layers of different structures, mineral pigments of different compositions and shapes were used, including clay, ground natural calcium carbonate and different types of precipitated calcium carbonates (PCC). With clay and the PCCs, samples having different average particle sizes were used. The modulus of coating layers based on some pigment blends was also evaluated and analysed.

2. Materials

The pigments used are described in Table I. Each pigment was dispersed in water with an anionic dispersing

TABLE I Shape and average size of pigments used

Pigment	Shape	Average size* (μm)
Clay A	Plate	2.4
Clay B	Plate	0.7
Clay C	Plate	0.4
Aragonite A (PCC)	Needle	2.7
Aragonite B (PCC)	Needle	2.6
Aragonite C (PCC)	Needle	0.6
Scalenohedral A (PCC)	Rosette	2.2
Scalenohedral B (PCC)	Rosette	2.1
Rhombic A (PCC)	Barrel	3.0
Rhombic B (PCC)	Barrel	1.0
Ground $CaCO_3$	Isometric	0.7

*Equivalent spherical diameter obtained from sedimentation experiments.

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TABLE II Values of E, E_v, E_0, V_p and V_p^{max} for the coating layers

Pigment	E (GPa)	E_v (GPa)	E_0 (GPa)	V_p	V_p^{max}
Clay A	3.5	5.4	5.7	0.35	0.50
Clay B	6.8	10	11	0.38	0.51
Clay C	3.0	4.9	4.7	0.39	0.52
Aragonite A	0.88	2.0	9.1	0.55	0.65
Aragonite B	1.2	2.2	3.9	0.46	0.59
Aragonite C	1.1	1.8	4.3	0.40	0.54
Scalenohedral A	0.61	0.8	4.5	0.49	0.60
Scalenohedral B	0.39	1.0	8.1	0.62	0.70
Rhombic A	0.65	1.4	6.5	0.53	0.63
Rhombic B	0.70	1.1	2.9	0.39	0.53
Ground $CaCO_3$	0.55	0.8	1.5	0.31	0.46

agent in the amount necessary to obtain a minimum viscosity: 10 parts of an anionic carboxylated styrene-butadiene (SB) latex and 1 part of carboxymethylcellulose (CMC) per 100 parts by weight of pigment were added. The glass transition temperature of the SB latex was 25° C [3]. Blends of clay B and ground $CaCO_3$, aragonite C or rhombic B were also prepared with latex and CMC. All suspensions were prepared at a total solids content of 50%.

3. Methods

Coating films were obtained by slow metering of the aqueous suspensions on to a polyethylene-coated aluminium foil. The films were then dried on the foil for ~ 30 min at 105° C. Provided that the film was sufficiently thick, the coating could be separated from the aluminium foil after drying. With this technique a series of coating layers with different thicknesses from ~ 30 to 70 μm were produced.

The elastic modulus in the plane of the coating was evaluated as the initial tangent modulus of stress–strain curves using a conventional tensile tester (Alwetron TCT 5, Lorentzen and Wettre, Stockholm, Sweden). The measurements were performed at 23° C and at a strain rate of 5.6×10^{-3} sec^{-1}.

The thickness of the coating layers was measured using the STFI thickness tester [5]. The porosity of the coating layers was calculated from the thickness and weight of the coatings and the densities of the coating components.

4. Results and comments

Table II shows the elastic modulus, E, of the coating films made from the different pigments. The clay-based coatings had the highest moduli, especially that based on clay B. This may be due partly to the orientation of the plate-like clay pigments in the plane of the film and partly to the high modulus of the clay itself. The porosity, V_p, of the films is also given in Table II and it can be noted that some of the PCC pigments give films of very high porosities, usually an indication of poor packing.

Within experimental error, the modulus values were not affected by the thickness of the films. Owing to the inhomogeneous nature of the films, the experimental scatter in the measured values of the modulus was rather high, of the order of 25%. The uncertainty in the porosity values is estimated to be $\sim 5\%$ of the values.

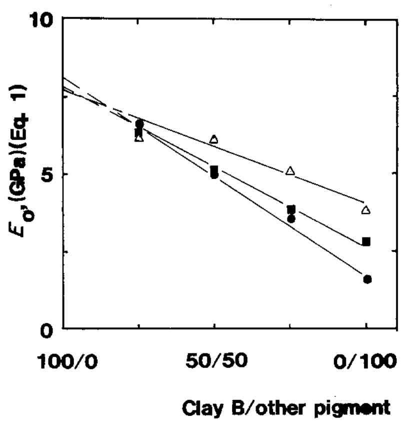

Figure 1 The modulus E_0 of the void-free coating layers based on pigment blends plotted against the pigment composition. (●) Clay B/ground $CaCO_3$, (■) clay B/rhombic PCC B, (△) clay B/aragonite C.

4.1. Effect of porosity on elastic modulus

The coating porosity is certainly expected to reduce the modulus of the films compared with that of the void-free material, due to the presence of non-load-bearing voids and to the effect of stress concentrations. Several empirical expressions have been proposed to account for the effect of the porosity, cf. [6, 7]. Recently, Bert [8] proposed the following expression

$$E/E_0 = [1 - (V_p/V_p^{max})]^{K_0 V_p^{max}} \qquad (1)$$

where E is the measured modulus of the coating films, E_0 is the modulus of the void-free film, i.e. without any pores, V_p is the porosity of the film and V_p^{max} is the "maximum porosity geometrically possible" [8]. The parameter K_0 is the stress concentration factor, which depends on the geometry of the voids, and it is listed in [8] for different pore geometries. Bert mentioned that Equation 1 underestimates somewhat the experimental values for E for porosities higher than 0.2.

In applying Equation 1 to the coating films it has been assumed that $K_0 = 2$, which corresponds to spherical voids, for films based on the calcium carbonates and the blends. The clay platelets in 100% clay coatings prepared from a well-dispersed suspension are highly oriented so that the interparticle voids are rather flat [9]. A K_0 value of 0.75 [8] was therefore used in this case. The maximum porosity, V_p^{max}, was calculated as corresponding to the sum of the void volume and of the volume of the SB latex and CMC.

Table II includes the calculated values of the modulus of the void-free material, E_0, and the values of V_p^{max}. Again, it can be noted that the calculated modulus value of the clay B film is rather high compared to the others. In general, the E_0 values of the coating layers are closer to each other than the measured E values. Table II also gives values of E_v, i.e. the modulus of the coatings where only the volume effect of the voids was accounted for (E_v is calculated simply as $E_v = E/(1 - V_p)$. These values are lower than the calculated E_0 values (especially for the $CaCO_3$-based coatings), which is to be expected because Equation 1 also accounts for the effect of stress concentrations.

Fig. 1 shows the E_0 values for the three types of blends used here as a function of the pigment composition. The values arrange themselves on separate straight lines. Extrapolation of these lines to a composition corresponding to a 100% clay B coating gives an E_0 values of ~ 7 to 8 GPa, which is somewhat lower than that given in Table II.

4.2. Applicability of composite theory

The void-free coating layer may be regarded as a material consisting of pigment particles in a polymeric matrix, although the volume fraction of the matrix, i.e. the SB copolymer, is rather low, ~20%. As an alternative to the approach of Bert, it may therefore be worthwhile to calculate E_0 using composite concepts. One way to estimate E_0 is to use the Halpin–Tsai equations [10]

$$\frac{E_0}{E_m} = \frac{1 + \eta \xi V_f}{1 - \eta V_f} \qquad (2)$$

with

$$\eta = \frac{E_f/E_m - 1}{E_f/E_m + \xi} \qquad (3)$$

Here E_f and E_m are the moduli of pigment and matrix, respectively, V_f the volume fraction of the pigment, and ξ a shape-dependent parameter. When applying Equation 2 it is assumed that the pigment particles are oriented mainly in the strain direction. Equation 2 also requires that the adhesion between the pigment and the SB matrix is perfect. This is, however, not a critical requirement because the degree of adhesion has no marked effect on small-strain properties such as the modulus, unless the degree of adhesion is exceedingly low [11, 12].

The $CaCO_3$-based coatings are considered first. For these pigments, which are not plate-like, the ξ-factor is set to be twice the aspect ratio of the particles. The elastic modulus of $CaCO_3$ is chosen to be 35 GPa [13]. For an SB copolymer with a glass transition temperature of 25° C, the elastic modulus can be estimated to be ~200 MPa [14]. From scanning electron micrographs it was estimated that the aspect ratio is about 1 for ground $CaCO_3$ and rhombic B, about 2 for rhombic A, about 3 for aragonite B and C and about 5 for aragonite A. The scalenohedral pigments had a complicated shape to which it is difficult to assign any aspect ratio and they were not considered in the subsequent analysis. The aspect ratio of the pigment is of importance with regard to the magnitude of the modulus. If, for example, the aspect ratio is increased from 3 to 4, the modulus of the composite will, in the present case, increase by ~20%.

For the clay pigments it is assumed that the aspect ratio is 10, because a typical clay platelet has a diameter of 1 μm and is 0.1 μm thick. For a clay pigment with this aspect ratio, a ξ-value of 6 [15] has been used and a value of 70 GPa for the modulus of clay has been found in the literature [15]. The Halpin–Tsai equations yield a value of ~ 6 GPa which is in rather good agreement with the E_0 value calculated for clay A and C, but lower than that noted for clay B, cf. Table II.

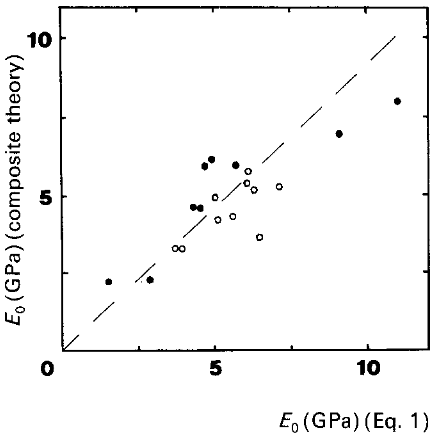

Figure 2 Comparison of the E_0 values for the coating layers calculated from composite concept Equations 2 or 4 and from Equation 1. Unfilled symbols refer to layers based on pigment blends, filled to layers based on one type of pigment.

For plate-like pigments, other models than the Halpin–Tsai equations have also been suggested, cf. [16] and a model proposed by Padawer and Beecher [17] has been tested. This gives the modulus E_0 of the void-free coating as

$$E_0 = (1 - V_f)E_m + E_f V_f(\text{MRF}) \qquad (4)$$

where

$$\text{MRF} = 1 - \frac{\tanh u}{u} \qquad (5)$$

and

$$u = \alpha \left[\frac{G_m V_f}{E_f(1 - V_f)} \right]^{1/2} \qquad (6)$$

Here G_m is the shear modulus of the SB polymer and α is the ratio between the diameter of the clay platelets and their thickness, i.e. the aspect ratio, which is assumed to be 10.

With this model a value of ~ 7 to 8 GPa is obtained which again is close to the values for clays A and C obtained using Bert's Equation 1, but considerably lower than that obtained for clay B. At present we have no explanation of the difference in stiffness between coatings based on clay B and the other two clay-based coatings.

Fig. 2 compares the E_0 values obtained from the composite theories with that obtained from Equation 1. Data for the coating films based on pigment blends are also included in this graph. There is considerable scatter in the graph but, considering the number of approximations which necessarily have to be made in an analysis of this type, the agreement can certainly be regarded as satisfactory.

5. Conclusion

It seems reasonable to conclude that the stiffness of the coating layer is determined in a predictable way by the porosity, the elastic moduli of the binder and the pigment, the amount of binder and the pigment shape. Thus it should be possible to maximize the bending stiffness of the coated paper in a controlled way by choosing the proper coating components. The analysis performed here supports the view that coating layers, being composite materials, can advantageously be analysed in terms of concepts developed within that field of solid mechanics.

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