

# Mechanical Properties of Clay Coating Films Containing Styrene-Butadiene Copolymers

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## Synopsis

The mechanical properties of clay-based pigmented coating films bonded with a series of carboxylated styrene-butadiene latex binders have been investigated. The in-plane tensile strength and the elongation at rupture increased with increasing amount of polymeric binder. It is suggested that this is due to an improvement in stress transfer through the structure. The mechanical behavior of the films was furthermore found to be strongly related to the properties of the polymeric binder at the usage temperature. In torsional pendulum experiments an increase in the glass transition temperature of the polymeric binder was observed when it was incorporated in the coating film. This is interpreted as being the result of a decrease in the segmental mobility of the polymer molecules due to the presence of the clay particles, i.e., due to the interaction between the clay pigments and the binder. The interaction was, however, less noticeable in experiments using an NMR (nuclear magnetic resonance) technique. If the clay was replaced by calcium carbonate, a strong interaction, as measured using NMR, was observed between  $\text{CaCO}_3$  and the styrene-butadiene polymer, although the in-plane mechanical strength and ductility were reduced. A structural model accounting for some of the observed differences in mechanical behavior between clay-based and  $\text{CaCO}_3$ -based coating films is suggested.

## INTRODUCTION

Pigmented coatings are used within the paper industry to improve the optical and printing properties of paper. The coating is applied as an aqueous dispersion to the surface of the paper and is often based on clay and contains a synthetic polymer as a binding material. For natural reasons, the properties of the coated paper depend to some degree on the properties and the structure of the coating, e.g., the surface strength of the coated paper is expected to be related to the ultimate properties of the coating itself. The structure of the pigmented coatings is rather complicated<sup>1-3</sup>; e.g. the porosity of the coatings may be of the order 30-35% and thus they cannot be considered as homogeneous materials. Within the polymer field, there appear to be only a few studies dealing with the properties of pigmented coatings bonded with different types of polymeric systems. The primary aim of the present communication is to report the results of an investigation into the ultimate and viscoelastic properties of the coating films themselves. In the majority of the tests, a series of styrene-butadiene lattices with different

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glass transition temperatures were used as binding materials. For comparison also poly(vinyl alcohol) was employed as binder in some cases. Some experiments using the nuclear magnetic resonance (NMR) technique were also carried out in order to gain knowledge of the degree of interaction between the pigment particles and the polymeric binder.

The mechanical behavior of filled polymers has been studied in great detail and has been summarized in textbooks and review articles; see e.g., Refs. 4-7. It has been shown that the mechanical properties of such composites are dependent on the shape and the size of the filler particles used, the stiffness of filler and matrix, the adhesion between filler and polymer, etc. However, it is not likely that a pigmented coating can be regarded as a "true" filled polymer, since the amount of polymer used is only of the order of 10% by weight. It cannot even be expected that the pigment particles are completely covered with the polymer. On the other hand, it can be expected that the mechanical properties of the polymer will, to a large degree, be reflected in the mechanical behavior of the coating film since the polymeric binder will take an active part in stress transfer within the structure. This is analogous to the situation encountered in networks of cellulose fibers bonded by small amounts of polymers.<sup>8</sup>

Since there is only a small amount of polymer in the coating film, it is more important that there is a sufficient degree of interaction between pigment particles and polymer (good adhesion) than is the case with filled polymers of a more conventional type. The degree of interaction is important not only for the mechanical performance of the coatings,<sup>9</sup> but also because printability improves with increasing interaction.<sup>10</sup> As shown below, this interaction also affects the viscoelastic properties of the coating film.

## EXPERIMENTAL

### Materials

Coating films based on English clay and bonded with different amounts of polymer latices were used in this study. Five carboxylated styrene-butadiene (SB)-based latices, with different glass transition temperatures ( $T_g$ ), were used as binders (see Table I). For comparison, the mechanical properties of pigmented coating films containing poly(vinyl alcohol) (PVOH) were also evaluated. In a series of experiments the clay was successively replaced by calcium carbonate and the mechanical properties were determined. In this case only one type of SB binder was used. Approximately

TABLE I  
Glass Transition Temperature  $T_g$  of the Pure Polymer Films

Polymer	$T_g$ (°C)
SB-1	-17
SB-2	3
SB-3	14
SB-4	25
SB-5	40
PVOH	~85

77% of the clay particles were smaller than 2  $\mu\text{m}$ , and the corresponding value for the carbonate particles was 90%.

The clay was dispersed in water containing 0.35 pph of a dispersant. The dry solids content of the final mixture (including latex) was ca. 60%. The coating films were cast on aluminum foil at room temperature and subsequently dried at 105°C for 30 min. Films of pure latex were made in a similar manner.

### Methods

**Mechanical Properties.** The mechanical properties of the films were measured with a conventional tensile tester at 23°C and 50% RH. The length of the coating film samples was 29 mm and the width 16 mm. The mechanical properties of the films were evaluated from measurements performed on coating films of different thicknesses and thus different basis weights. Since the mechanical properties depend on the thickness (basis weight), the results have, unless otherwise stated, been reduced to a constant basis weight (50 g/m<sup>2</sup>) by means of regression analysis. The corresponding thickness of the films is of the order of 30  $\mu\text{m}$ .

**Dynamic Mechanical Properties.** The glass transition temperature ( $T_g$ ) and the temperature dependence of the stiffness of the polymeric binders as well as the pigmented film were determined using a Torsional Braid Analyzer operating at ca. 1 Hz. The measurements were performed in a nitrogen atmosphere.

**ESCA.** The ESCA spectrometer used was a Leybold-Heraeus device with Al K $\alpha$  radiation ( $h\nu = 1486 \text{ eV}$ ).

**Nuclear Magnetic Resonance (NMR).** NMR has in several investigations been used as a tool to study the effects of interaction between polymers and fillers. It is generally assumed that interaction between polymer and filler results in a decrease in the segmental mobility of that part of the polymer which is closest to the surface of the fillers. The proton spectra of polymer samples loaded with filler therefore display two, or possibly several, line components of different widths at temperatures somewhat above the glass temperature of the polymer. For the systems mainly investigated here, where clay constitutes the main component, a broad line component is also present originating from the protons of the filler. For systems of a similar kind where a soft polymer component is present only to a small extent, wideline NMR, utilizing phase-sensitive detection, makes possible accurate study of the properties of this soft component.<sup>11,12</sup> Independently of the properties of the rigid components in other respects, the properties of the soft component are here interpreted from the intensity and the line width of the narrow line component in the NMR spectrum.

## RESULTS AND DISCUSSION

### Influence of Polymer Content on Mechanical Properties

Figure 1 shows the effect of polymer content on the tensile strength ( $\sigma_B$ ) and the elongation at rupture ( $\epsilon_B$ ) for coating films based on clay. In this case, polymer SB-2 (Table I) with a  $T_g$  value of 3°C was used as a binder. An increase in the polymer content from 9 to 17% by weight thus improves

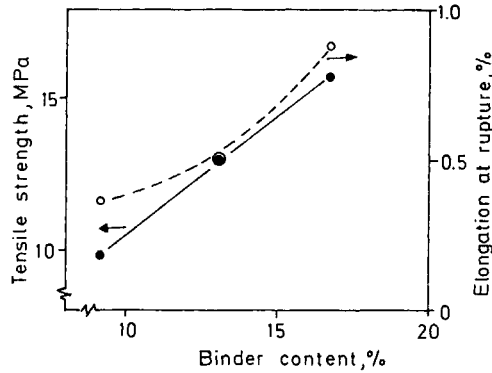


Fig. 1. The tensile strength (filled symbols) and the elongation at rupture (unfilled symbols) of clay-based coating films vs. the amount of binder SB-2.

both strength and ductility of the films. This improvement is especially marked in the  $\epsilon_B$  value, which is more than doubled from less than 0.4 to 0.9% over this range of polymer content. This behavior is perhaps expected since addition of binder should provide a better stress transfer throughout the deformed coating.<sup>7</sup> It should be noted that pigmented coating films in general have a very low ductility compared with conventional filled polymers.<sup>3,4</sup> The tensile modulus ( $E$ , stiffness) also increases when the binding level is raised.

The mechanical data shown in Figure 1 have been reduced to a constant basis weight ( $75 \text{ g/m}^2$ ); the corresponding thickness is ca.  $45 \text{ }\mu\text{m}$ .

### Mechanical Properties of Coating Films with Different Binders

In a series of experiments, the mechanical properties of clay-based coating films containing 9% of a number of polymeric binders were evaluated. Five different styrene-butadiene-based lattices were chosen as binders and also a grade of poly(vinyl alcohol). The  $T_g$  values of the polymers, as determined by the torsional braid measurements, are given in Table I. In Figure 2 the tensile strength and the elongation at rupture of the pigmented films are plotted vs. the  $T_g$  value of the binder. In general, the tensile strength increases when the  $T_g$  value is increased, i.e., the "softer" the binder is, the lower the strength of coating film. At higher  $T_g$  values there is a tendency

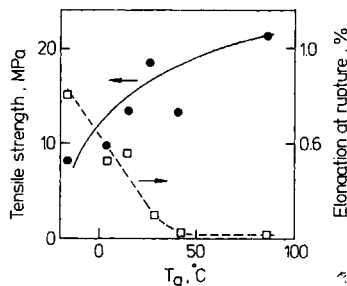


Fig. 2. The tensile strength and the elongation at rupture of clay-based coating films vs. the  $T_g$  value of the binder. Binder content 9% by weight.

for the strength values to approach some kind of plateau, which would indicate that utilization of binders with still higher  $T_g$  values will not be a very effective way to raise the tensile strength. The tensile modulus  $E$  of the coating films increases with the glass transition temperature of the binders in a similar way as the tensile strength. Thus the mechanical properties are to a large degree determined by the properties of the binder, i.e., the binder plays a very active part in the transfer of stress in the deformed film. This behavior is analogous to the situation encountered with bonded cellulosic networks.<sup>7</sup>

Figure 2 also shown the elongation at rupture for the pigmented coatings films vs. the  $T_g$  value of the polymers used. The lower the  $T_g$  value, i.e., the more rubberlike the binder is at the test temperature, the higher the  $\epsilon_B$  value. For binders with a glass transition temperature above room temperature, the elongation at rupture is very low ( $<0.1\%$ ). These polymers are normally rather brittle under such conditions and the noted behavior is thus to be expected. This is probably also the reason for the levelling off of the tensile strength at higher values of the glass transition temperature. Again, the properties of the binder have a very strong influence on the ductility of the coating films.

### Properties of Coatings Based on Clay and $\text{CaCO}_3$ and Bonded with Styrene-Butadiene Copolymers

Figure 3 shows the tensile strength and elongation at rupture in the plane of films based on mixtures of clay and calcium carbonate. In this case a styrene-butadiene-based polymer with a glass transition of  $3^\circ\text{C}$  (SB-2) was used as a binder. The polymer content was ca. 9%. Evidently, the introduction of  $\text{CaCO}_3$  into the coating films reduces both the strength and ductility. The influence on  $\epsilon_B$  is rather dramatic; for a coating based only on  $\text{CaCO}_3$  the  $\epsilon_B$  value is of the order of 0.1%, whereas for a clay-film it is ca. 0.5%. The strength is reduced to a somewhat smaller extent, by a factor of 2. The stiffness also decreases in a similar fashion (not shown in the figure).

To analyze to some extent the binder distribution in coating films of this

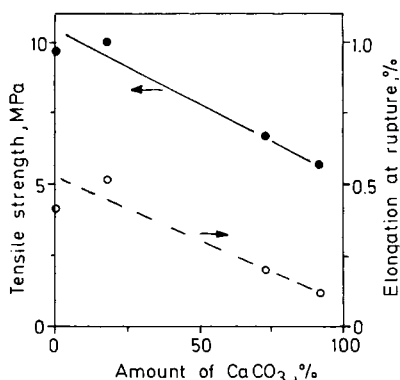


Fig. 3. The tensile strength and the elongation at rupture of a series of coating films with different proportions of clay and  $\text{CaCO}_3$ .

kind, an ESCA study was performed on the films. To obtain a qualitative measure of the influence of the binder and of  $\text{CaCO}_3$ , the heights of characteristic peaks of the ESCA spectrum, such as, e.g.,  $\text{C}_{1s}$  and  $\text{O}_{1s}$ , were compared. In this case, the ratio of the peaks corresponding to O and C as well as the ratios of the C— to the Ca— and Si— peaks were evaluated. These ratios, corresponding to the surface of the coating films, are shown vs. the amount of  $\text{CaCO}_3$  in the coatings in Figure 4. The ratio O/C decreases markedly when increasing the amount of  $\text{CaCO}_3$  in the coating films. If the surface layers of the film are carefully polished away and the ESCA analysis is performed on the exposed "surface," the decrease in the ratio O/C, as the amount of  $\text{CaCO}_3$  increases, is significantly more pronounced. This decrease in the O/C ratio, as measured using ESCA, is larger than what is expected due to the increase in the amount of C as  $\text{CaCO}_3$  is added. This behavior suggests that  $\text{CaCO}_3$  and clay do not interact with the styrene-butadiene in the same way and that the  $\text{CaCO}_3$  particles are more covered with the polymer than the clay. This increased coverage of the particles does not, however, improve the stress transfer in the plane of the coating structure (cf. Fig. 3).

As expected, the C/Si ratio increases strongly when the amount of  $\text{CaCO}_3$  added to the coating film is increased. Figure 4 also includes the ratio C/Ca. This ratio decreases when more  $\text{CaCO}_3$  is added, down to a value of ca. 1 when the coating film is based on calcium carbonate alone.

#### Viscoelastic Properties of Clay-Based Coating Films Bonded with Different Styrene-Butadiene-Based Polymers

Dynamic mechanical analysis is a very important technique within polymer science for the determination of glass transition temperatures and for the evaluation of the temperature dependence of the stiffness of materials. Normally the mechanical loss factor ( $\tan \delta$ ) exhibits a maximum when it is plotted against temperature in the primary transition region of a polymer, and the temperature at which this maximum occurs is often taken as a measure of  $T_g$ . In Figure 5, the mechanical loss factor is shown vs. the temperature for one of the styrene-butadiene copolymers (SB-2) as

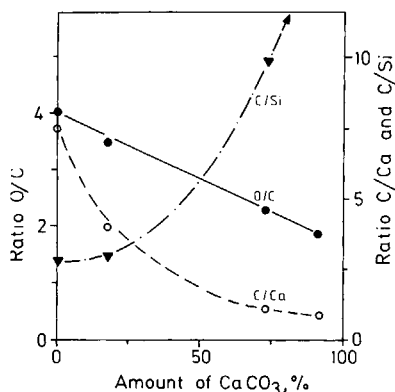


Fig. 4. Results from the ESCA analysis. The ratios O/C (●), C/Ca (○) and C/Si (▼) vs. the amount of  $\text{CaCO}_3$ . Binder: 9% SB-2.

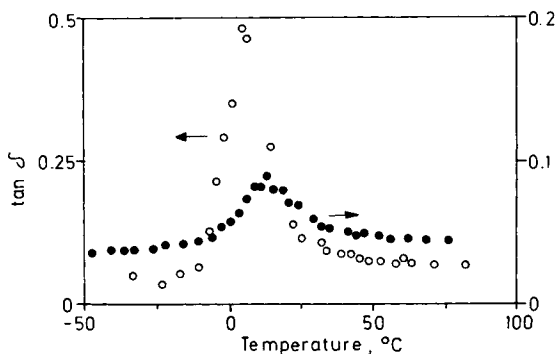


Fig. 5. The mechanical loss factor  $\tan \delta$  for the (○) pure polymer (latex SB-2) and for the (●) clay-based coating film containing 9% SB-2 vs. the temperature.

well as for a clay film bonded with the same material. For the pure polymer the maximum in  $\tan \delta$  is very clear whereas for the coating film the intensity of the peak is lower since the amount of polymer is low (ca. 9%). It is, however, clearly discernible, and this indicates that the binder plays an active part in the stress transfer.<sup>8</sup>

It should be noted that the  $T_g$  value of the polymer in the film is slightly higher than the value for the pure binder. This behavior was observed for most of the styrene-butadiene binders used in this study, although in some cases the shift was only a few degrees. Table II gives the shift in  $T_g$  of the polymers when used as binders. The  $T_g$  values have been determined using the torsional braid analyzer, and the amount of binder was in all cases ca. 9%. Behavior of this kind has been reported in many situations for filled polymers<sup>6,7,13-16</sup> and is often correlated to the polymer-filler interaction. A high degree of interaction corresponds to a higher shift in  $T_g$ . The shift in  $T_g$  results from a reduction in segmental mobility of the macromolecules close to the surface of the pigments provided the degree of interaction is sufficiently strong.<sup>13-17</sup> As has been pointed out by Theocaris and co-workers,<sup>13,18,19</sup> composites can in many cases be modeled as three-layer materials, with an interlayer or interphase, between the filler (pigment in this case) and the matrix (or binder), with properties different from those of the filler and the matrix. The introduction of the interphase concept can qualitatively account for the increase in  $T_g$  of the coatings, as observed in this work. Though it thus is plausible that the mechanical properties of the

TABLE II  
Glass Transition Temperatures of the Styrene-Butadiene Polymers in the Pure State and As Measured in the Coating Films

Polymer	$T_g$ (pure) (°C)	$T_g$ (coating film) (°C)
SB-1	-17	-15
SB-2	3	12
SB-3	14	18
SB-4	25	26
SB-5	40	45

coating films can be described using the three-layer model, it is, at present, not especially meaningful to carry out any detailed analysis in terms of this model since the required parameters are not known for the types of coatings considered here. No doubt an approach along these lines is likely to be very fruitful in future since deeper analysis of the mechanical behavior of pigmented coating films are utmost important.

The volume of the polymer which is restrained by the pigment can be estimated from the increase in  $T_g$ . According to Droste and Dibendetto,<sup>20</sup> the shift in  $T_g$ ,  $\Delta T_g$ , can be expressed as

$$\Delta T_g = \Delta T_{g\infty} [1 - \exp(-B\phi)] \quad (1)$$

where  $\Delta T_{g\infty}$  is the maximum increase in  $T_g$ ,  $\phi$  is the volume fraction of the filler (pigment), and  $B$  a constant related to the strength of interaction between polymer and pigment. According to eq. (1) and to experimental results,  $\Delta T_g$  tends towards a plateau level as the amount of filler is increased.<sup>5,17</sup> The filler content at which  $\Delta T_g$  levels off is denoted  $\phi_m$  and it can be related to the thickness of the binder layer restrained by the polymer ( $\delta$ ) by the expression

$$\phi_m = 1/(1 + S\delta) \quad (2)$$

where  $S$  is the specific surface area of the filler (pigment). In order to estimate  $\delta$ , the shift in  $T_g$  at various binder levels must therefore be evaluated. This was not done in this work, but a rough estimate of the layer thickness can be obtained by assuming that the  $\Delta T_g$  shift has reached its maximum value at a binder level of 9% by weight. The value  $S \approx 30 \text{ m}^2/\text{cm}^3$  for the specific surface area of the clay gives a value for  $\delta$  of ca. 80 Å, which is of the same order of magnitude as obtained with other systems.<sup>16</sup>

The  $\tan \delta$  measurements indicate that there is an interaction between the binder and the pigment which assists the stress transfer mechanism and also affects the properties of the binder. The effect of interaction is noticeable not only in the  $T_g$  shifts but also in the temperature dependence of the stiffness of the coating films. Figure 6 shows the variation with

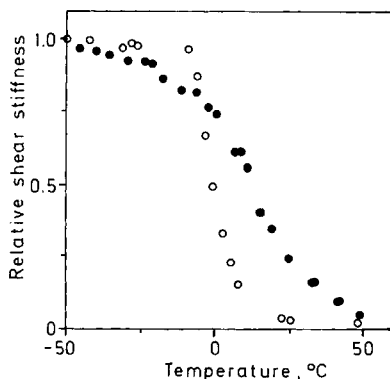


Fig. 6. The effect of temperature on the shear stiffness of the (●) pure polymer (latex SB-2) and of the (○) clay-based coating film containing 9% SB-2.



temperature of the torsional stiffness of a pure styrene-butadiene binder (SB-2) and that of a coating film with the same binder. The stiffness scale has been expanded in order to include the main features of the curve. The values of the stiffness are thus only relative values. When the polymer passes through  $T_g$ , its rigidity decreases rather sharply. This is true both for the pure polymeric system and for the polymer in the coating film as can be seen in Figure 6. The transition region is, however, significantly broader for the polymer when it is inside the film, i.e., the relaxation time spectrum has broadened. Again this is due to the partial restriction of the polymer chains close to the pigment surface (cf. also Ref. 17).

It should be mentioned that a few preliminary tests on the dynamic mechanical behavior of  $\text{CaCO}_3$ -based films were also made. A similar shift in  $T_g$  as for the clay films was noted.

### Nuclear Magnetic Resonance (NMR) Studies

A high segmental mobility of the macromolecules (above  $T_g$ ) in general gives rise to a narrow line component of the spectrum, whereas in the glassy state broad resonance lines are observed. The ratio of the intensity of the broad line to that of the narrow line component is here used as a measure of the decrease in segmental mobility of the macromolecules (constituting the binder) induced by the pigment particles present. An increase in this ratio thus corresponds to an improved degree of interaction between the two phases.

In these experiments SB-2 (9%) was used as the polymeric binder and either clay or  $\text{CaCO}_3$  constituted the pigment particles. The pigmented films were normally dried as before, i.e., at  $105^\circ\text{C}$  for 30 min. The remaining water was eliminated by drying at room temperature over  $\text{P}_2\text{O}_5$ . In the case of the clay-based films, the NMR spectrum, when compared to that corresponding to the pure binder, revealed only a slight decrease in the segmental mobility. This behavior contradicts to some extent the result obtained with the dynamic mechanical analysis, where a clear increase in  $T_g$  was observed in some cases. This point is not clearly understood at present. It should be pointed out that if the heating time is extended at  $105^\circ\text{C}$ , the broad-line/narrow-line intensity ratio increases significantly, indicating that the heat treatment is of great importance for the interaction between the clay and the binder.

However, when  $\text{CaCO}_3$  is used as pigment, a strong effect on the ratio of the broad-line to narrow-line intensities is observed. In Figure 7 this ratio is shown for pure SB-2 coating films which have not been dried at high temperatures (water removed by drying over  $\text{P}_2\text{O}_5$ ) and for coating films which have been dried at  $105^\circ\text{C}$  for 30 min. The binder level was 9%. The NMR spectra were recorded at  $40^\circ\text{C}$ . Evidently, there is no significant difference between never-dried coating films and the pure binder with regard to the broad/narrow ratio. The drying however brings about a strong increase in the ratio, i.e., the segmental mobility of the polymer chains has been substantially reduced. The flow behavior of the binder is thus important in order to establish a high degree of interaction between the two phases. Further drying at  $105^\circ\text{C}$  up to 24 h increases the ratio, but the

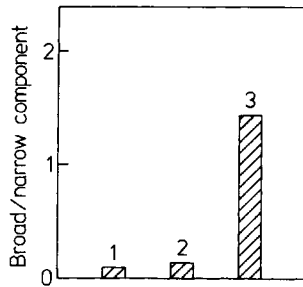


Fig. 7. The broad-line/narrow-line ratio according to the NMR analysis for  $\text{CaCO}_3$  films bonded with 9% SB-2: (1) pure SB-2; (2) coating film dried at room temperature; (3) coating film dried at 105°C for 30 min.

change from 30 min to 24 h is less dramatic than the effects shown in Figure 7.

### FINAL REMARKS

The major findings arrived at in this communications can be summarized as follows:

—An increase in binder content leads, as a consequence of improved stress transfer, to a stronger and more ductile coating film. This refers to the in-plane properties.

—The mechanical properties of the pigmented clay-based films are to a large extent determined by the properties of the binder at the usage temperature despite the low amount of polymer used.

—The dynamic mechanical analysis of the clay-SB systems indicates that the segmental mobility of the macromolecules is restricted due to the presence of clay particles. However, the NMR study reveals only a small interaction between the two components.

—The NMR data indicate a strong interaction between calcium carbonate and the styrene-butadiene latex provided that films have been dried at 105°C for 30 min.

The first two results above are, in view of the behavior of similar systems, e.g., bonded cellulosic networks, to be expected. The shift in  $T_g$  is likewise no surprise and can be described by the interlayer concept.<sup>13</sup> However, the behavior of the clay-based coating films compared with that of films based on  $\text{CaCO}_3$  deserves some additional comments. First it should be noted that the pigments differ in shape. The clay particles are platelike, whereas the  $\text{CaCO}_3$  particles have a more spherical shape. The ESCA analysis indicated that the binder covered the  $\text{CaCO}_3$  particles better than was observed for the clay particles, and the degree of interaction between pigment and SB latex was higher in the case of  $\text{CaCO}_3$  as revealed by the NMR data. The higher degree of coverage of the  $\text{CaCO}_3$  with the binder can perhaps be traced to the different wettability behavior of the two pigments. Clay can be considered to have a high energy surface, while the surface energy of  $\text{CaCO}_3$  is considerably lower.<sup>21</sup> The critical surface tensions of the binders (SB) are markedly lower than those of the pigments which indicates that the pigments should be wetted by the SB binders. However, clay is consid-

ered to be a hydrophilic pigment while  $\text{CaCO}_3$  has a more hydrophobic character.<sup>21</sup> The critical surface tension of hydrophilic high-energy surfaces is known to be significantly reduced by the presence of moisture.<sup>22</sup> At sufficiently high humidities, the critical surface tensions can be reduced down to values which are of the same magnitude as the binders used here.<sup>22</sup> Considering that all coatings were prepared from aqueous dispersions, the difference in coverage between clay and carbonate is perhaps not too surprising. It can also be noted that in some cases it has been mentioned that the degree of adsorption on the pigments of the different components in a coating color is higher in the case of  $\text{CaCO}_3$  than for clay,<sup>21</sup> which is attributed to their different degree of hydrophobicity.

However, when  $\text{CaCO}_3$  is introduced as a pigment into the films the in-plane mechanical properties gradually deteriorate, i.e., clay-based films are in general stronger and more ductile. In printing operations, on the other hand,  $\text{CaCO}_3$  films are often from experience considered to be somewhat stronger. In this case, as well as in the measurement of the "pick resistance" of the coated paper, the load is applied perpendicular to the plane of the paper. Thus it is the mechanical properties in the thickness direction of the coating and the adhesion of the coating (or binder) to the paper which here determines the performance. On a structural level, a simple model which may to some extent describe the observed differences between clay-based and  $\text{CaCO}_3$ -based coating films may be proposed. The model is schematically presented in Figure 8.

First it should be observed that there is a major difference in pigment shape between the clay and  $\text{CaCO}_3$  particles. The clay particles are platelike while the  $\text{CaCO}_3$  particles have a more spherical shape. During the coating process the clay particles are oriented parallel to the surface of the paper (or as in this case the aluminum foil). For a polymeric composite containing oriented platelike fillers, it is known that the mechanical properties of the composite in the direction of the oriented fillers is higher than for a composite containing spherical fillers.<sup>4</sup> The properties in the transverse direction are, however, not improved to any larger extent. It is now obvious that the difference in particle shape can explain the difference in mechanical behavior between the clay-based films and the  $\text{CaCO}_3$  coatings (cf. Fig. 3).

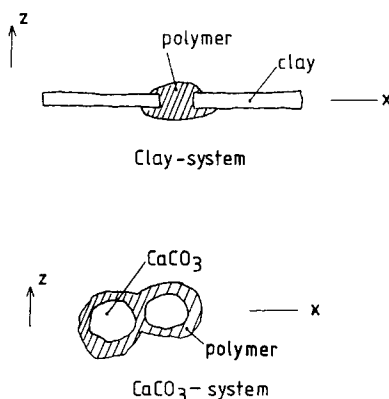


Fig. 8. Schematic models of the clay-binder structure and of the  $\text{CaCO}_3$ -binder structure.

However, the difference in binder distribution in the two types of coatings may also be of importance in this context. The spherical  $\text{CaCO}_3$  particles are assumed to be rather uniformly covered with the binder (cf. the ESCA results), while the platelike clay particles are not covered to the same extent. With the clay the binder is more confined to regions "between" the particles, thus assuring a sufficient stress transfer in the plane, but there is a smaller amount of binder in the thickness direction between the particles. The  $\text{CaCO}_3$  particles are assumed to be covered to a greater extent, which improves the strength (and pick resistance) in the  $z$ -direction. The effective amount of polymer in the plane is consequently reduced, and thus the in-plane strength and ductility are also lower. This model is also consistent with the idea that a  $\text{CaCO}_3$ -based film requires a smaller amount of binder than clay in order to meet the demands of the printing operation. The high degree of interaction between  $\text{CaCO}_3$  and SB is probably also important in this context. Thus both the difference in particle shape and the difference in the degree of binder coverage of the pigments can account for the observed mechanical behavior of coating films based on clay and  $\text{CaCO}_3$ .

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