

# Heterogeneous Latices as Binders in Porous Particle Structures

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**ABSTRACT:** Heterogeneous carboxylated styrene-butadiene (S/Bu) latices were prepared by a two-stage polymerization process, using three seeds of polystyrene with different molecular weights. The second-stage polymer was a copolymer with a fixed S/Bu-ratio of 1 and a methacrylic acid (MAA) content of either 1 or 10 wt %. It has been found that the morphology of the films made from these latices influenced the modulus in the rubbery region of these films. The heterogeneous latices were used as binders in porous structures based on micron-sized kaolin particles. Such structures are typically employed as paper coatings. Polyester substrates were coated with aqueous suspensions containing the kaolin particles and the heterogeneous latex. The coatings were dried at room temperature, which corresponds to the rubbery region of the latex films. It was found that a higher modulus (which is determined here by the morphology of the latex film) in the rubbery region of the films was associated with coating layers with higher porosity, greater light scattering ability, and higher coating gloss. This is interpreted as being the result of a retarded shrinkage of the coating layers during the drying of these structures due to the increase in modulus of the latex films. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 661–670, 1997

**Key words:** binders; latex; minerals; paper coating; porosity

## INTRODUCTION

Coatings to improve the surface characteristics and the print quality of paper and board are porous structures built up of micron-sized mineral particles. A synthetic polymer latex is, in most cases, used to ensure a sufficient cohesion of this structure and also to anchor the thin coating layer to the paper substrate. Styrene-butadiene (S/Bu) latices are very common for this application. These latices are normally carboxylated by incorporating small amounts (up to 10%) of vinyl acids, which improve the adhesion between the latex and the mineral pigment or the paper substrate.<sup>1,2</sup>

In order to provide the required cohesive properties of the structure, the binder must have a rather low film-forming temperature, normally of the order of 0–25°C. Films of these latices are then quite ductile at room temperature, which is beneficial for the surface strength of the coated material, e.g., the danger of coating rupture during subsequent printing on the paper is reduced.<sup>3</sup> A polymer with high ductility and a rather low Young's modulus is thus favorable for the surface strength of the coated material. On the other hand, the use of a polymeric binder with a lower modulus improves the surface strength at the expense of the bending stiffness, which is another important property of the coated product. In order to achieve a proper balance between the surface strength and the stiffness properties of the coated

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product, Takahashi et al.<sup>4</sup> used heterogeneous latices of the core-shell type as binders in coating layers. The latices were based on S/Bu but were designed to have a hard core with a softer shell to give the proper combination of film-forming ability and stiffness.

Besides influencing the mechanical properties of the coating layer, the use of heterogeneous latices can yield advantages with regard to other important characteristics of the coated material. When the paper is coated, a mineral-based aqueous suspension (coating color) is metered onto the paper surface. The water leaves the structure through evaporation and drainage to the absorbing substrate, and the coating consolidates into a dry and porous layer. At a certain solids concentration during the drying, the solid particles come in contact with each other, i.e., they cannot settle any more, the water film on the coating layer breaks up, and the gloss of the wet coating layer decreases sharply with increasing solids concentration. This solids concentration has been denoted FCC ("first critical concentration") by Watanabe and Lepoutre<sup>5</sup> and depends on the composition of the suspension. The shrinkage experienced by the coating layer after FCC until the layer is dry is, in a sense, considered to produce negative effects. For example, a higher degree of shrinkage may reduce the ability of the coating layer to cover the substrate and the light scattering efficiency of the structure to deteriorate due to a decrease in porosity of the layer. Furthermore, the mineral pigment particles are reorientated during the shrinkage (from FCC) of the coating layer, and this increases the surface roughness of the coating layer and reduces its gloss. The binder has been found to have a marked influence on the shrinkage. The lower its modulus, the more extensive is the flow of the polymeric material, and this increases the degree of shrinkage.<sup>5,6</sup>

It follows that polymeric particles with a high film-forming temperature will yield coating layers with a high gloss but with rather low mechanical cohesion. Lee<sup>7</sup> then suggested that the use of latices of the core-shell type with a softer shell than core could be used to achieve a proper balance between the surface properties and the mechanical performance of the layers, and his experimental results were, on the whole, in line with his expectations. The higher gloss obtained with the heterogeneous latices than with a homogeneous type of similar composition can be attributed to

the smaller degree of shrinkage of the coating layer during its consolidation.

In his work, Lee<sup>7</sup> indicated that the morphology of the heterogeneous latex particles (with a given composition) could have a substantial influence on the mechanical properties of the latex films and on the function of the latices as binders in porous structures, such as coating layers. This is the subject of the present article.

Heterogeneous latex particles with different particle morphologies can be prepared by multi-stage emulsion polymerization processes (see, for example, Karlsson et al.<sup>8</sup>). In this work, which can be regarded as one of a series of reports,<sup>9,10</sup> heterogeneous S/Bu latices have been prepared by a two-stage emulsion polymerization, using different types of styrene seed particles (the core), a fixed ratio between the amounts of butadiene and styrene, and varying amounts of methacrylic acid (MAA) for the carboxylation in the second-phase polymer (the shell). The morphologies of the latex films and their viscoelastic properties have been described in detail elsewhere,<sup>10</sup> and, consequently, only the most important features are given here. In the present study, attention has been focused on the effect of the morphology (and the mechanical properties) of the latex films on the structure and surface properties of the porous mineral-based layers used as paper coatings. The influence of these latices on the rheological properties in the low shear rate region of the corresponding mineral suspensions is also reported. It is of course essential that incorporation of latices of this type does not have any negative impact on the flow properties of the mineral suspensions, since this would impair the processability of the system.

## EXPERIMENTAL

### Materials

#### Latices

The heterogeneous carboxylated S/Bu latices were prepared by a two-stage emulsion polymerization process described in detail elsewhere.<sup>9</sup> Three different types of styrene seed latex were used as the core. In the shell, the ratio of butadiene to styrene was fixed, and different amounts of methacrylic acid were used as a functional monomer.

Seed A was an unmodified polystyrene (PS) dispersion. In seed B, the molecular weight of the

**Table I Compositions of the Latices**

Latex	A1	A10	B1	B10	C1	C10	R1	R10
Seed	A	A	B	B	C	C	—	—
MAA (wt %)	1	10	1	10	1	10	1	10
S (wt %)	49	45	49	45	49	45	48	44
Bu (wt %)	50	45	50	45	50	45	51	46

seed polymer was reduced by the use of carbon tetrachloride ( $\text{CCl}_4$ ) as a chain transfer agent. In seed C, 90% of the total monomer was charged prior to the polymerization. The last 10% of the monomer was a mixture of divinyl benzene (DVB) and styrene at a DVB/S-ratio of 0.04. The DVB/S was added at the end of the polymerization in order to obtain cross-linked shells of the seed particle having residual double bonds.

The second-stage polymerization was performed as a seeded batch process.<sup>9</sup> The ratio of the seed to the stage two monomer in all the polymerizations was 1 : 1. The second-stage polymer was poly(butadiene-*co*-styrene-methacrylic acid) (Bu/S/MAA) with a fixed Bu/S-ratio of 1 and an MAA-content of either 1 or 10 wt %.

Two latex samples having the same overall composition as the second-stage polymer were prepared as references (denoted R1 and R10). These polymerizations were performed as batch processes under the same conditions as the second-stage polymerizations. The second-stage polymer and the reference latex compositions, as well as the notations used hereafter, are given in Table I. Table II gives the particle diameters of the latices (obtained by transmission electron microscopy) and the weight average molecular weights of the seed polymers as measured by gel permeation chromatography.<sup>10</sup>

**Table II Latex Particle Size and Seed Molecular Weight**

Latex	Particle Size (nm)	Seed $M_w$ ( $/10^3$ )
A1	124	1300
A10	120	1300
B1	135	230
B10	119	230
C1	188	1350 (>4000) <sup>a</sup>
C10	179	1350 (>4000) <sup>a</sup>
R1	160	—
R10	100	—

<sup>a</sup> A polymer fraction above the exclusion limit of the column system.

### Other Components

A paper coating grade of kaolin clay (Speswhite, English China Clay International Ltd., Cornwall, United Kingdom) was used as the pigment throughout this study. The particle size distribution of this grade is quite broad, with 61% of the particles having an equivalent spherical diameter of less than 2.0  $\mu\text{m}$  (from sedimentation experiments). The BET (nitrogen) area was 10.5  $\text{m}^2/\text{g}$ , according to the manufacturer.

A low molecular weight sodium polyacrylate (Dispex N40, Allied Colloids Ltd., Bradford, United Kingdom) was used as dispersing agent for the pigment. The amount of dispersant used was 0.25% relative to the weight of the kaolin clay.

The water retention aid, sodium carboxymethyl cellulose (NaCMC), was delivered from Metsä-Serla Chemicals Oy, Äänekoski, Finland (Finnfix 5). The degree of substitution was 0.72 according to the manufacturer. The amount of NaCMC used in the suspensions was 1 part per 100 parts (by weight) of the pigment (pph).

### Methods

#### Preparation of the Coating Colors (Mineral-based Suspensions)

The coating colors were prepared in a conventional manner from the concentrated and dispersed pigment suspension. NaCMC and, subsequently, the latex were added to the suspensions, and, thereafter, the pH-value was adjusted to 8.5. The colors were allowed to equilibrate overnight, and the pH was then again adjusted to 8.5 (if required). The colors thus contained 1 pph NaCMC and 10 pph latex, and the solids content was 53.5% in all cases.

#### Rheological Measurements

A rheometer (Bohlin VOR, Bohlin Reologi AB, Lund, Sweden) with a coaxial cylinder geometry (Couette system) was used to evaluate the flow

curves in shear and the dynamic-mechanical properties of the suspensions at 25°C. The viscosity and the shear stress were measured up to a shear rate ( $\dot{\gamma}$ ) of 1500 s<sup>-1</sup>. The flow curves were fitted to the Bingham equation, as follows:

$$\tau = \tau_o + \eta_{pl} \dot{\gamma} \quad (1)$$

where  $\tau$  is the shear stress,  $\tau_o$  is the Bingham yield stress, and  $\eta_{pl}$  is the plastic viscosity. The storage shear modulus  $G'$  and the mechanical loss factor ( $\tan \delta$ ) were determined at a frequency of 1 Hz.

### Properties of Dry Coating Layers

Coating layers were drawn down on polyester films with a bench coater (K-coater, RK Print-Coat Instruments Ltd., Royston, United Kingdom) using wire-wound rods. The coating layers were dried at room temperature, and their (dry) coat weight varied between 23 and 68 g/m<sup>2</sup>.

The thickness of the coatings (on the polyester films) was measured between spherical platens using a thickness tester developed at STFI, Stockholm, Sweden.<sup>11</sup> This method gives an integrated mean thickness. The densities of the coating layers were evaluated from the slope of the straight line obtained when the coat weight was plotted as a function of the thickness of the layers. The densities of the coatings could then be converted into porosities, since the coating formulation and the densities of the components were known.

The light scattering coefficient ( $s$ ) of the dry layers was evaluated as a function of the wavelength of light (400–700 nm) using the Kubelka–Munk theory from the measured reflectance factors of the coated polyester film over a black and over a white background. These measurements were made with an Elrepho 2000-instrument (Datcolor, Zürich, Switzerland). An uncoated polyester film was placed over the backgrounds when the reflectance factors of the two backgrounds were measured. This procedure minimized the effects of the plastic substrate and made it possible, in principle, to estimate the  $s$ -value of the coating layer only.

Gloss measurements on dry coating layers were performed with a Lehmann LGDL-07 gloss meter according to Tappi Test Method T480.

**Table III The Glass Transition Temperatures of the Latices<sup>a</sup>**

Latex	Soft Phase $T_g$ (°C)	Hard Phase $T_g$ (°C)
A1	-10	102
A10	24	103
B1	-29	97
B10	18	101
C1	-13 & 25	104
C10	13 & 25	102
R1	0 & 23	—
R10	6 & 24	—

<sup>a</sup> See Hagen et al.<sup>10</sup>

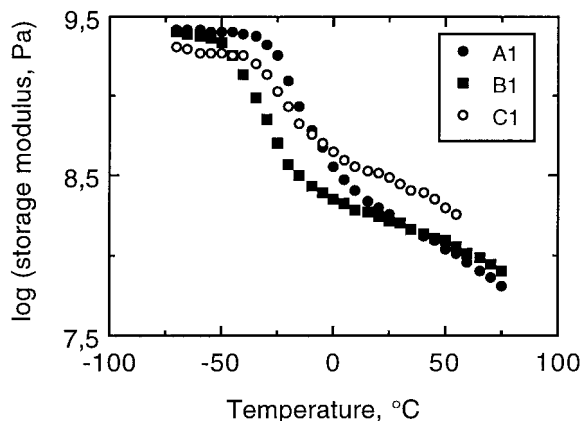
## RESULTS AND DISCUSSION

### Morphology and Dynamic–Mechanical Properties of Films Based on Pure Latices: A Summary

The morphology and the dynamic–mechanical properties (in tension) of films based on the pure latices, i.e., without addition of the mineral pigment and the other chemicals, have been described in detail by Hagen et al.<sup>10</sup> Their findings are summarized in the following.

Using transmission electron microscopy, it was possible to divide the six films based on the different heterogeneous latices into three groups. In the latex films based on the pure latices A1 and B1, the PS seed formed hemispheres, which were distributed in the matrix of the second-stage polymer (S/Bu/MAA). The hard PS particles appeared to be clustered and formed a network throughout the structure with the particles contacting each other. Latices A10 and B10 exhibited close to core-shell morphologies with the second-stage polymer surrounding the seed particles. In the films, the PS seed particles were evenly distributed in the matrix of the copolymer. In the latex particles C1 and C10, small occlusions of the second-stage polymer were observed to be included in the seed particles. The seed particles had a quite irregular shape, and in the film they formed a more or less continuous network through particle–particle contacts. Films made from latices C1 and C10 were brittle, and the latices exhibited a poorer film-forming capability than the other types. The films from the reference latices R1 and R10 were soft and rubber-like.

The dynamic–mechanical analysis of the latex films exhibited several interesting features. Table III summarizes the values of the glass transition



**Figure 1** Storage modulus as a function of temperature for pure films based on latices A1, B1, and C1.<sup>10</sup>

temperature ( $T_g$ ) as determined from the position of the maximum in  $\tan \delta$  at a frequency of 1 Hz (for the second-stage polymer). The glass transition temperature of the seed polymer was determined with differential scanning calorimetry.

The glass transition temperature of the second-stage polymer increased from  $-10$  to  $24^\circ\text{C}$  for the latices A when the MAA content was increased from 1 to 10%. This increase was suggested to be due to the hydrogen bonding capability of MAA.<sup>12</sup> The rubbery modulus was, in general, higher for film A1 than for that based on latex A10, which was attributed to the interparticle contacts in the former structure. At room temperature, the storage modulus was approximately the same for both the films (A1 and A10).

The soft phase in film B1 exhibited quite a low  $T_g$  value. It was suggested that this was due to a reduction in molecular weight of the second-stage polymer by the presence of residual  $\text{CCl}_4$ .<sup>10</sup> The storage modulus at room temperature of film B1 was also somewhat (but not very much) lower than that of the film based on latex A1. The temperature dependence of the storage modulus of film B10 was similar to that of the film based on the latex A10.

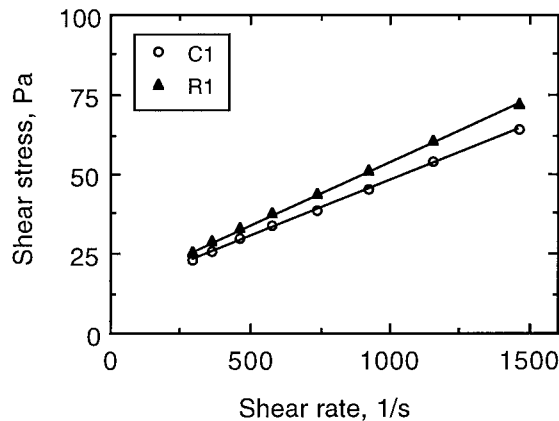
Films based on latices C1 and C10 exhibited two peaks when the mechanical loss factor  $\tan \delta$  was plotted as a function of the temperature  $T$  (Table III). The lower of these temperatures corresponded to the main decrease in storage modulus as the temperature increased. The second-stage polymer thus formed two phases in these films. Hagen et al.<sup>10</sup> suggested that the higher transition temperature should be associated with occlusions of the second-stage polymer near or at the surface of the seed particles. The higher tran-

sition temperature may be due to grafting of this fraction to the PS seed, and a compositional drift of the seeded copolymerization may also be of importance in this context. Figure 1 shows that films based on latex C1 had a significantly higher storage modulus in the rubbery region than the films based on latices A1 and B1. It was suggested that this might be due to the irregularly shaped residues of the cross-linked seed particles, which formed a load-bearing network throughout the structure. The immobilized occlusions may also contribute to this behavior. Similarly, the storage modulus of the film C10 was higher than that of the films based on latices A10 and B10 in the rubbery region.

The reference films R1 and R10 also exhibited two peaks in their  $\tan \delta(T)$ -curves. Hagen et al.<sup>10</sup> attributed the peak at higher temperatures to a compositional drift in the polymer formed as the polymerization proceeded, and this peak then corresponded to a phase that was comparatively rich in MAA and styrene. An important observation in this connection was, however, that the storage modulus (for both R1 and R10) at room temperature was approximately two orders of magnitude lower than that of the films based on the heterogeneous latices. Film R10 had a somewhat higher modulus than film R1 over a temperature region extending from 0 to  $75^\circ\text{C}$ .

### Rheological Properties of the Coating Colors

Figure 2 shows the flow curves, i.e., the shear stress versus the shear rate up to ca  $1500 \text{ s}^{-1}$ , for the kaolin-based suspensions containing the latices C1 and R1. These curves are typical for



**Figure 2** The shear stress as a function of shear rate for the kaolin-based suspensions containing the latices C1 and R1.

**Table IV Rheological Properties of the Kaolin-based Suspensions**

Latex	$\tau_o$ (Pa)	$\eta_{pl}$ (mPas)	$G'$ (Pa)	$\delta$ (degrees)	$\gamma_{cr}$
A1	15.8	34.2	107	5.9	0.015
A10	13.8	34.4	94	5.6	0.018
B1	14.2	35.0	105	5.6	0.011
B10	16.6	33.8	102	6.0	0.014
C1	12.9	35.5	74	6.4	0.012
C10	12.8	35.3	70	7.1	0.013
R1	14.8	39.7	93	6.5	0.013
R10	16.3	35.2	102	6.0	0.020

the flow behaviour of the suspensions used here. There was obviously a linear relation between the shear stress and the shear rate, which can be described by the Bingham equation [eq. (1)]. The experimentally determined yield stress and the plastic viscosity of the suspensions are given in Table IV.

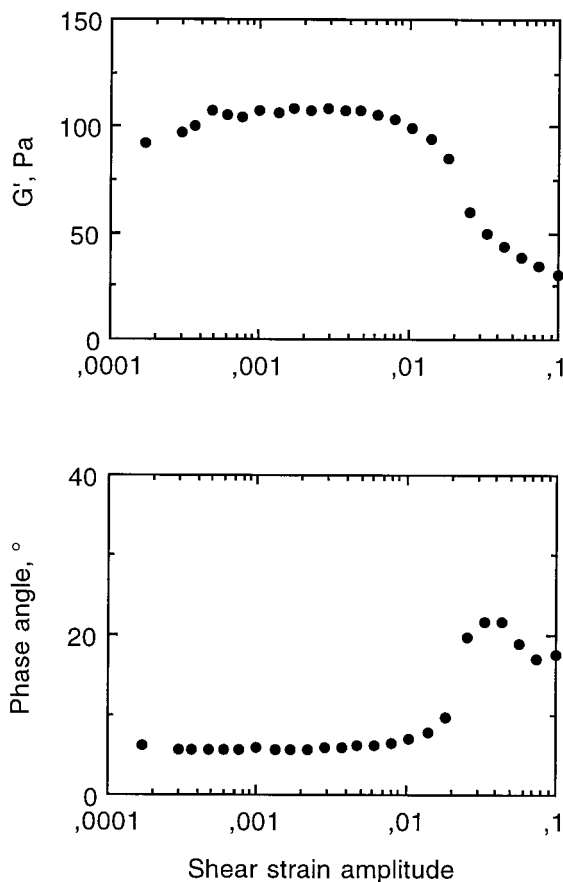
The flow properties in shear were not markedly dependent on the type of latex used in the suspension. In fact, the viscosity in the investigated shear rate region was quite similar to that noted for suspensions of similar kinds containing a commercial homogeneous S/Bu latex.<sup>13</sup> Somewhat lower values of the yield stress can be noted for the suspensions containing latices C1 and C10, but the differences are not great. It may be that the larger particle diameter of these latices is to some extent responsible for these lower values (see, for example, Johnson and Kelsey<sup>14</sup>).

The suspensions are viscoelastic at low deformation rates, and Figure 3 shows the storage modulus  $G'$  and the phase angle  $\delta$  as functions of the shear strain amplitude applied when performing the dynamic-mechanical measurements on the suspension containing latex A1. The frequency was 1 Hz.

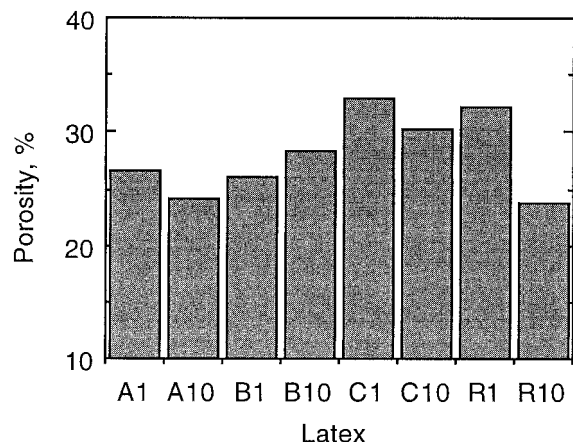
The storage modulus and the phase angle were approximately independent of the shear strain amplitude up to a certain critical value at which  $G'$  started to decrease markedly and  $\delta$  increased. This strain value is denoted by  $\gamma_{cr}$  and marks the limit of the linear viscoelastic regime of the suspensions. It corresponds to a gradual deterioration of the structure of the suspension as the deformation is increased. The storage modulus, the phase angle (in the linear viscoelastic region), and the critical strain for the different suspensions are tabulated in Table IV. Again, no great differences due to the choice of latex can be noted, although the storage moduli of the suspensions

containing latices C1 and C10 were somewhat lower than was noted for the others.

The magnitude of the storage modulus of the suspensions is quite similar to that of a corresponding suspension containing a commercial S/Bu latex, but the phase angle is slightly (a few



**Figure 3** The storage modulus  $G'$  and the phase angle  $\delta$  versus the shear strain amplitude for the kaolin-based suspension containing the latex A1. The frequency was 1 Hz.



**Figure 4** The porosities of the dry coating layers containing the different latexes.

degrees) lower.<sup>15</sup> The suspensions containing the commercial (and homogeneous) latex grade, in general, also exhibited a somewhat higher critical strain. If this parameter is regarded as a measure of the strength of the wet structure, this means that the latexes used in this work produce a somewhat weaker wet coating structure. The general observation seems to be, however, that the incorporation of a heterogeneous latex does not significantly change the rheological properties in the low shear rate region compared to the properties obtained with latexes typically used in the field of paper coating.

#### The Porosity and Light Scattering Ability of the Dry Coating Layers

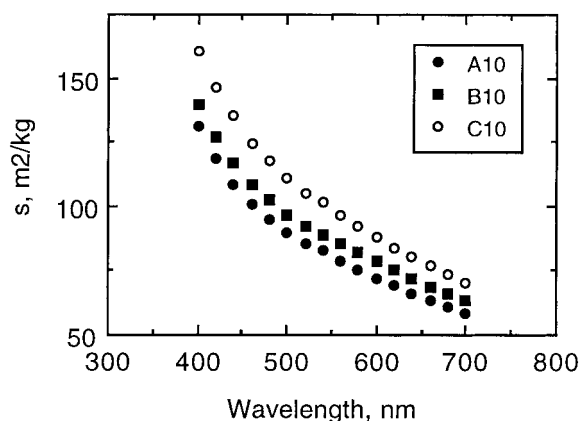
The porosities (or pore volumes) of the coating layers determined from measurements of the thickness and the coat weight of the dry layers on a polyester film are summarized in Figure 4.

The porosities are in the range of 20 to 35%, which is quite typical for coating layers of this kind.<sup>16,17</sup> Measurements of this kind are subjected to some experimental uncertainty, and there seem to be only small differences between the layers containing the latex systems A and B. The magnitudes of the moduli of the corresponding latex films were also quite similar at room temperature, which is the temperature at which the coatings consolidate. Coating layers containing latexes C1 and C10 exhibited higher porosities, which is paralleled by their higher stiffness (storage modulus) at room temperature. The coating layer containing the reference latex R10, which is a soft polymer, had the lowest porosity of the layers

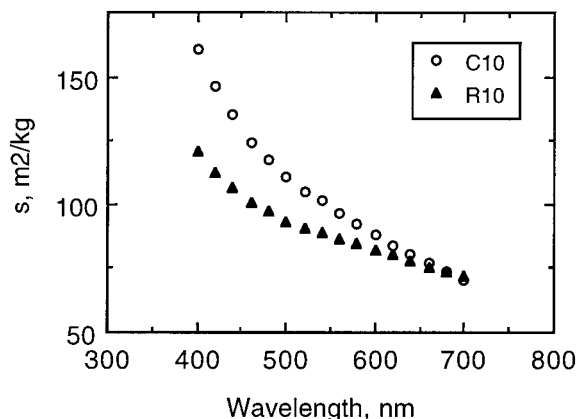
studied here. The rather high porosity of the layer with the soft reference latex R1 is however difficult to explain, and this result is not, in fact, in complete harmony with other physical properties of this layer (see below).

The light scattering coefficient ( $s$ ) of the coating layers decreased with increasing wavelength of light, as shown in Figure 5. In this case, the layers contained latexes A10, B10, or C10, and the coat weight of the layers was approximately 25 g/m<sup>2</sup>. The  $s$ -values of the coating layers containing A10 and B10 were quite similar to each other, which is in agreement with the rather similar porosities and storage moduli of the respective latex films at room temperature. The coating layer based on latex B10 actually had the higher porosity of these two, and this may be the reason for its somewhat higher  $s$ -value. When the stiffer latex C10 was used as binder in the coating layer, the light scattering ability of the coating was clearly higher.

When the heterogeneous latexes containing 1% MAA were used as binders, the  $s$ -value of the corresponding coating layers decreased somewhat (3–5 m<sup>2</sup>/kg), but the same relative order in light scattering efficiency was noted between the different layers, i.e., the layers containing latex C1 exhibited significantly higher  $s$ -values than those containing A1 or B1. It is possible that the decrease with decreasing MAA content in light scattering efficiency (which certainly is only minor) reflects a change in the degree of interaction between the polymer and the mineral pigment due to the change in the degree of carboxylation (see also Heiser<sup>1</sup>). In comparison with the heteroge-



**Figure 5** The light scattering ability of the dry coating layers containing the latexes A10, B10, or C10 as a function of the wavelength of light. The coat weight was ca 25 g/m<sup>2</sup>.



**Figure 6** The light scattering ability of the dry coating layers containing latices C10 and R10 as a function of the wavelength of light. The coat weight was ca 25 g/m<sup>2</sup>.

neous latices, the reference latices R1 and R10 gave coating layers whose  $s$ -values were on the lower side; for example, the  $s$ -values at a wavelength of 400 nm were 131 and 121 m<sup>2</sup>/kg, respectively. The light scattering ability of the coating layer containing latex R1 may still be regarded as quite high, but it is lower than could be expected from its porosity (Fig. 4).

The wavelength dependence of the light scattering coefficient indicated that there was a significant difference in structure between the coating layers containing the heterogeneous latices and those in which the reference latices were used as binders. Figure 6 is an example of this. The decrease in the light scattering coefficient of the layer containing the reference latex R10 with increasing wavelength was not as pronounced as that of the layer with latex C10. The layer containing latex R1 exhibited a similar behaviour. Gate<sup>18</sup> has suggested that the wavelength dependence of  $s$  can be described as follows:

$$s = \alpha \lambda^{-\beta} \quad (2)$$

where  $\alpha$  is a constant,  $\lambda$  the wavelength of light, and  $\beta$  a parameter that depends on the average pore size of the structure. A smaller value of  $\beta$  corresponds to a larger pore diameter. The results obtained here thus indicate that the heterogeneous latices produced structures with a smaller average pore dimension than the reference latices. This difference may be a consequence of the presence of the seed particles in the heterogeneous latices and the resulting difference in film-

forming behaviour of these latices and the reference systems.

Some similarities with results from sintering polystyrene particles in coating structures were evident. Lepoutre and Alinec<sup>19</sup> made kaolin-based coating layers containing polystyrene particles by a draw-down technique. After being dried at room temperature, these layers were sintered, i.e., the temperature was raised in order to form a film of the initially discrete polymeric particles. The film forming of the polystyrene particles resulted in an increase in the pore size of the coating structure.

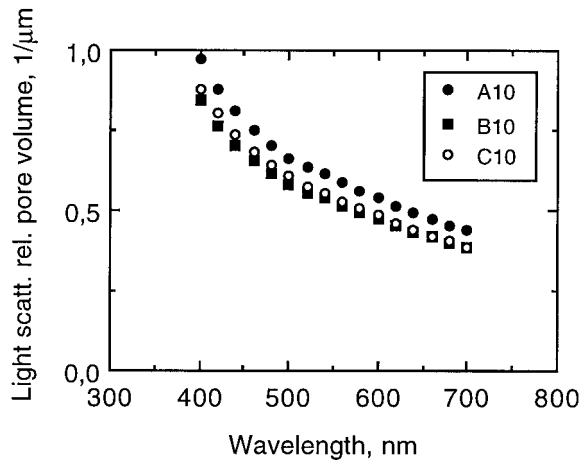
Since the pore volume was in most cases larger in the coating layers containing the heterogeneous latices; at the same time, as the average pore size was smaller, it can be concluded that the number of pores must be substantially larger in those layers. The average pore size in the coating layers containing the heterogeneous latices appeared to be of the same order of magnitude since the slopes of the corresponding linear relations between  $\log s$  and  $\log \lambda$  were rather similar.

From an optical point of view, the coating structure can be considered to be a solid matrix containing voids that are the scattering sites. The light scattering efficiency of the pore structure is then in a sense better described if the light scattering is expressed in relation to the pore volume (or void volume) than in terms of area per unit mass as is done in Figures 5 and 6. The light scattering coefficient relative to the pore volume ( $s_m$ ) can be expressed as

$$s_m = s \rho_s (1 - \varepsilon) / \varepsilon \quad (3)$$

where  $\rho_s$  is the density of the solid phase of the dry layer only, and  $\varepsilon$  is the porosity of the layer. A value of  $\rho_s = 2.35$  g/cm<sup>3</sup> was used here for all the layers. Figure 7 shows the wavelength dependence of  $s_m$  for coating layers containing latices A10, B10, and C10. The light scattering efficiency relative to the void volume was not very different for these layers (including those containing A1, B1, and C1). This indicates that the effectiveness of the pores in these layers with regard to their ability to scatter light is rather similar (which is quite reasonable since the average pore sizes of the different layers are approximately the same) and that the differences in their  $s$ -values are primarily associated with the differences in porosity. When a comparison is made with the layers containing the reference latices, there is, however, also a difference in average pore size, which ac-





**Figure 7** The light scattering coefficient relative to the pore volume of the coating layers containing the latices A10, B10, and C10 as a function of the wavelength.

counts to some extent for the different light scattering ability of those layers.

### The Gloss of the Coating Layers

It was mentioned in the introduction that a potential advantage of using heterogeneous latices in coating layers is that the shrinkage (from FCC) of the layers as the water leaves the structure as the layer dries is counteracted. This is due to the stiff core (seed particles) of these latices. The results with regard to the porosity and the light scattering ability indicate that such a reduction in shrinkage is achieved. Furthermore, a reduction in the shrinkage of the kaolin-based layers as they consolidate often results in a smoother and glossier coating surface, which is desirable from an applications point of view. Figure 8 shows the gloss of the coating layers on the polyester film. These layers have not been subjected to any post-treatment, e.g., calendering, after drying.

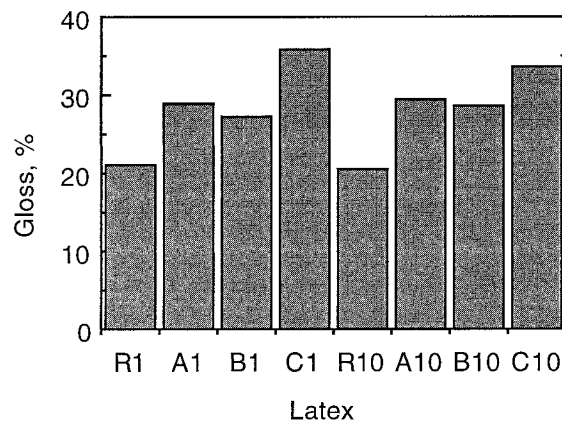
Obviously, the morphology of the latices had a strong influence on the gloss of the coating layers. The homogeneous and readily film-forming reference latices R1 and R10 gave the coatings with the lowest gloss levels. The gloss increased due to the higher stiffness at the consolidation temperature when the reference latices were replaced by latices A or B. There was no substantial difference between the A and B systems, nor did the degree of carboxylation appear to play a major role. This reflects the fact that the stiffness (the storage modulus) of these latices does not differ signifi-

cantly at room temperature, i.e., the consolidation temperature. Films based on C1 or C10 had the highest storage modulus at room temperature, and the corresponding coating layers also exhibited the highest gloss levels. Although the latex composition (with regard to the second-stage polymer) was the same, latex system C gave a gloss which was approximately 75% higher than that of the layers containing reference latex R. This is interpreted here in terms of a smaller shrinkage due to the greater stiffness of the heterogeneous latices.

The gloss values of the coating layers containing the heterogeneous latices appear to compare very well with results obtained with commercially available carboxylated S/Bu-latices. For example, the gloss of similar draw-downs on polyester film of coating colors containing such a commercial latex has been reported to be 27–28%.<sup>20</sup> This is lower than the gloss of the coating layers containing latex C.

### CONCLUSIONS

It has been shown that heterogeneous latices can provide advantages when used as binders in paper coatings. The porosity, the light scattering ability, and the gloss of the layers were improved compared with the performance of a single-phase (or homogeneous) latex. These results also suggest that the covering ability of the coating layer will be improved with this type of polymeric binder. This is important for the print quality of the coated paper.<sup>21</sup> It appears likely that the presence of the hard seed particles in the latex is associated with these improvements. It is less likely



**Figure 8** The gloss of the dry coating layers containing the different latices.

that the improvements should be attributed to a change in the degree of interaction between the components of the coating color in the wet state since the rheological properties of the different suspensions were quite similar.

The hard phase in the polymeric binder increases the stiffness of the latex but does not, in the ideal case, affect the film-forming ability of the second-stage polymer, which is essential for the development of sufficient mechanical ductility of the coating film. A plausible conclusion is that the shrinkage of the coating layer is retarded by the hard seed particles (which are unaffected by film formation). An adequate magnitude of the storage modulus in the rubbery region of the polymer is essential to reduce and control the shrinkage during the consolidation of the coating layer. It is known that binders or homogeneous pigments (like polystyrene particles), which exhibit no substantial flow during the consolidation of the coating layers, retard the shrinkage of the coating layers and promote the gloss.<sup>6,7</sup> On the other hand, such layers tend to be quite brittle, something that can perhaps be avoided by using heterogeneous latices with a softer shell with suitable film-forming properties.

The results reported here show that the morphologies of heterogeneous latex particles of a given composition are also of considerable interest. The morphology has a substantial effect on the stiffness of the polymeric material in the rubbery region and also on the structure and properties of the corresponding coating layer. It is interesting here that latex particles A10 and B10, which had almost perfect core-shell morphologies, were not the most effective ones. Instead, the irregularly shaped seed particles in latex films C1 and C10 provided benefits in the form of a higher storage modulus of the latex films as well as improvements in gloss and light scattering ability of the kaolin-based coating layers. The reason for this improved performance can be traced to a greater reinforcing effect of these particles, probably due to residual seed particle contacts throughout the polymeric structure (Hagen et al.<sup>10</sup>).

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