Influence of Particle Surface Properties on Film Formation from Precipitated Calcium Carbonate/Latex Blends

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ABSTRACT: The surface properties of films prepared from a blend of precipitated calcium carbonate pigment (PCC) and poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) [P(BMA/BA); $T_g = 0°C$] latex were investigated in terms of the surface characteristics of the PCC and P(BMA/BA) latex particles. It was found that the presence of carboxyl groups on the P(BMA/BA) latex particles significantly improved the uniformity of the distribution of the PCC particles within the P(BMA/BA) copolymer matrix and the gloss of the resulting films. This phenomenon could be explained by an acid-base reaction between the PCC particles and the carboxylated P(BMA/BA) latex particles. Studies on the influence of the composition of PCC/P(BMA/BA) latex blends on the gloss and transparency of the films were also performed, which led to the determination of the critical pigment volume concentration (CPVC) of this system, which was found to be 42 vol %. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 891–900, 2002

Key words: blends; films; dyes/pigments; latexes; interfaces

INTRODUCTION

In the formulation studies, it was found that the opposing ζ-potential values of the PCC particles (positive) and the P(BMA/BA) latex particles (negative) was the reason that stable PCC/P(BMA/BA) latex blends could not be obtained if no stabilizer is added. The addition of sodium polyacrylate (NaPA) to the PCC slurry changed the ζ-potential of the PCC particles from positive to negative, resulting in the formation of a stable PCC/P(BMA/BA) latex blend.

In latex coatings applications, pigments and extenders are added to a latex binder to achieve desired gloss, opacity, and color. Pigments can be organic or inorganic. In this article, film formation of blends of inorganic pigment and latex binder was studied. The inorganic pigment used in this work is precipitated calcium carbonate pigment (PCC) and the latex binder is poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) [P(BMA/BA)] latex. As calcium carbonate pigments are heavily used in paper coatings,[1,2] the surface properties of the calcium carbonate pigmented latex films are very important.[3] Thus, academic research aimed at gaining an understanding of the relationship between various film formation parameters and the properties of calcium carbonate pigmented latex films has been triggered. Of greatest interest in this research program is the study of the surface morphology and the surface properties of films obtained after drying blends of precipitated calcium carbonate pigment and P(BMA/BA) latex. One focus of this work is the investigation of the influence of carboxyl groups that were present on the P(BMA/BA) binder particles on the surface properties of the PCC/P(BMA/BA) blend films.

Although stabilizers are widely used in the formulation of pigmented latex coatings,[4–6] academic research on the mechanism through which the pigment stability is increased by the presence of suitable stabilizers is very limited. However, formation of a stable pigment/binder blend is a prerequisite for obtaining pigmented latex films and the investigation of the film properties. In this article, the effect of adding sodium polyacrylate (NaPA), which is commonly used in coatings formulations in preparing stable PCC/P(BMA/BA) latex blends, was investigated.

EXPERIMENTAL

Materials

n-Butyl methacrylate (BMA; Aldrich; reagent grade), *n*-butyl acrylate (BA; Aldrich; reagent grade), and methacrylic acid (MAA; Aldrich; reagent grade) monomers were used. All monomers were cleaned by passing them through an inhibitor removal column (Aldrich). Anionic and cationic ion exchange resins (AG 1-X4 and
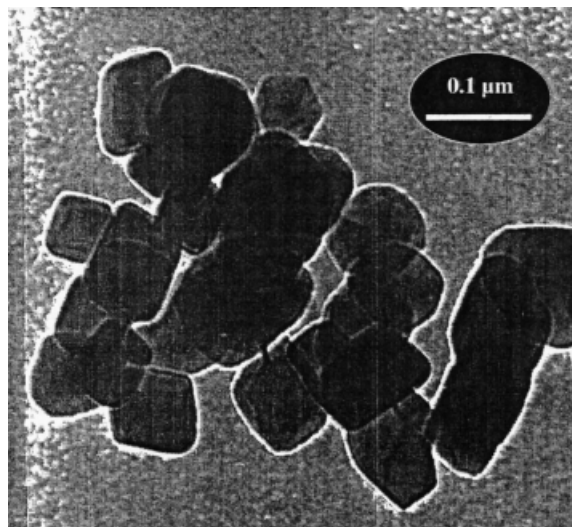

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Figure 1 TEM micrograph of the precipitated calcium carbonate pigment particles.

AG 50W-X4, 20–50 mesh; Bio-Rad Company) were treated by the method described elsewhere.[7] Volumetric hydrochloric acid (HCl; 0.02 N; LabChem Inc.; analytical grade), volumetric sodium hydroxide (NaOH; 0.02 N; Fisher Scientific; analytical grade), potassium persulfate (KPS; Fisher; reagent grade), sodium dodecyl sulfate (SDS; Fisher; reagent grade), sodium hydroxide (NaOH; Fisher; reagent grade), ammonium hydroxide (NH$_4$OH, 28 wt % NH$_3$; EM Science), sodium polyacrylate (NaPA, MW = 5100 g/mol; Aldrich; reagent grade), and precipitated calcium carbonate (PCC; slurry of 14.4 wt % solids content in aqueous medium; equivalent particle size ~100 nm; Specialty Minerals) were utilized as received. A TEM micrograph of the PCC slurry is shown in Figure 1.

Synthesis of carboxylated P(BMA/BA) latex particles

Poly(n-butyl methacrylate-co-n-butyl acrylate) [P(BMA/ BA); carboxylated and noncarboxylated] latexes were synthesized using a monomer-starved semicontinuous emulsion polymerization process.[8] A 500-mL four-neck flask with an attached reflux condenser and nitrogen gas inlet tube was used to perform all syntheses. Also used were a PTFE stirrer blade (~230 rpm), and two feed tubes for surfactant solution and monomers. The reaction temperature was kept constant at 80°C. A BMA/BA mixture (BMA/BA = 75/25 wt/wt) comprised of about 10% of the total monomer used was introduced into the reactor in the seeding stage. After 1.5 h (95% conversion of seed monomers), the BMA/BA/(MAA) monomer mixture, consisting of approximately 90% of the total weight of the monomer used, and surfactant solution were separately fed into the reactor at constant rates using two syringe pumps (Harvard Apparatus 22). The ratio of BMA to BA fed was adjusted to obtain a desired T_g of 0°C using the equation of Pochan et al.[9] The characteristics of the resulting latex particles are listed in Table I.

Preparation of latex films

A specific amount of NaPA was added to 10 g of PCC to bring the stabilizer level to 0.5 wt % (based on the weight of solid calcium carbonate). The low glass transition temperature (T_g) latex, whose pH value was adjusted to ~9.0 using ammonia, was then added dropwise to the PCC–NaPA dispersion to produce a PCC/latex blend. The dispersions with 25 wt % solids content were drawn down on a glass microslide substrate (VWR) as well as on a plastic substrate (Leneta; sintered plastic sheets; BASF) using 3-mil and 6-mil

TABLE I
Characteristics of the PCC Pigment Particles and Latex Particles Used to Prepare PCC/P(BMA/BA) Latex Blend

Particle	PCC	P(BMA/BA)					
$D_n{}^a$ (nm)	86.3[f]	128.9	124.3	129.1	129.5	126.6	123.2
$D_w{}^b$ (nm)	135.5[f]	134.5	128.6	130.8	137.7	128.9	127.3
PDI[c]	1.57	1.043	1.035	1.013	1.063	1.018	1.033
Wt % MAA[d]	—	0.00	0.98	1.00	3.00	5.60	6.00
$\sigma_{COOH}{}^e$ (%)	—	0.00	6.75	7.58	14.20	21.78	33.34
pH	9.0	2.17	2.38	2.26	2.33	2.18	2.38
T_g (°C)	—	−1.68	−3.08	−0.96	−2.86	−0.88	−3.18

[a] Number-average particle diameter.
[b] Weight-average particle diameter.
[c] Polydispersity of particle size (= D_w/D_n).
[d] Based on the weight of the P(BMA/BA) copolymer.
[e] The particle surface area covered by carboxyl groups, choosing the cross-sectional area of each carboxyl group as 9 A^2 based on a theoretical calculation.[10]
[f] Measured by light scattering with 0.76 wt % NaPA present (based on the solid weight of PCC particles); calculation from the specific surface area of the PCC particles yielded a particle size of approximately 100 nm in diameter.

draw-down bars, respectively. The films were air-dried at 22°C and 50% relative humidity for 2 days.

Characterization

Surface gloss and transparency were measured with a Glossmeter (Novo-Gloss, Phopoint) at an incident angle of 75° and a Densitometer (X-Rite; Model 48), respectively. Each film was measured at three different points on the film surface, and at least two films were measured for each sample to obtain the average gloss value and standard deviation.

Surface morphology was analyzed with an atomic force microscope (AFM; Thermomicroscopes, Bio-Probe Electronics Module). The intermittent-contact mode was utilized for the film samples cast from PCC pigmented latexes. Transmission electron microscope (TEM) experiments to image the PCC particles were carried out using a Philips EM400T at an acceleration voltage of 100 kV. The PCC slurry of 14.4 wt % solids content was diluted with deionized (DI) water and dried on a copper grid and then observed under TEM.

ζ-Potential was measured using the Coulter DELSA 440 instrument (Coulter Company). A Coulter EMPSL 7 mobility standard (carboxyl-modified polystyrene latex particles in 0.01 M sodium phosphate buffer at pH 7.0) was employed for verifying the instrument and software. A PCC slurry of 14.4 wt % solids content was diluted with the serum from the original PCC slurry that was prepared by centrifuging the original PCC slurry and separating out the serum (IEC HI Centrifuge; International Equipment Company). Conductivity measurements were carried out with an YSI conductivity meter [Model 32; Yellow Springs Instrument (YSI) Co., Inc.] with a platinum-immersion type of electrode [Model: YSI 3403; Yellow Springs Instrument (YSI) Co., Inc.], which has a cell constant of 1.0 cm^{-1}. The pH of the latex blends were measured using a pH meter (Corning; model pH-30). The particle size and particle size distribution were measured by capillary hydrodynamic fractionation (CHDF, Model 1100; Matec Applied Sciences) and dynamic light scattering (Nicomp Submicron Particle Sizer, Model 370). All measurements were performed at room temperature (22°C).

RESULTS AND DISCUSSION

Formulation of precipitated calcium carbonate/latex blends

Unlike the PS/P(BMA/BA) latex blends studied in the previous publications,[11,12] which can usually be pre-

TABLE II
Summary of the Formulation Study Used to Prepare PCC/P(BMA/BA) Latex Blends

PCC			P(BMA/BA)					
pH	NaPA %[a]	SDS %	pH	Base	NaPA %[a]	SDS %	COOH	Results
~9	0	0	2.0	—	0	0	No	Coagulated
~9	0	0	2.0	—	0	0	Yes	Coagulated
~9	0	0	~9	NH$_4$OH	0	0	No	Coagulated
~9	0	0	~9	NaOH	0	0	No	Coagulated
~9	0	0	~9	NH$_4$OH	0	0	Yes	Coagulated
~9	0	0	~9	NaOH	0	0	Yes	Coagulated
~9	0	0	2.0	—	0	2.0	No	Coagulated
~9	0	0	2.0	—	0	2.0	Yes	Coagulated
~9	0	0	~9	NH$_4$OH	0	2.0	Yes	Coagulated
~9	0	0	~9	NaOH	0	2.0	Yes	Coagulated
~9	0	2.0	~9	NH$_4$OH	0	2.0	Yes	Coagulated
~9	0	2.0	~9	NaOH	0	2.0	Yes	Coagulated
~9	2.0	0	~9	NH$_4$OH	2.0	0	Yes	Stable
~9	2.0	0	~9	NaOH	2.0	0	Yes	Stable
~9	0.4	0	~9	NH$_4$OH	0.4	0	Yes	Stable
~9	0.4	0	~9	NaOH	0.4	0	Yes	Stable
~9	0.4	0	~9	NH$_4$OH	0.4	0	No	Stable
~9	0.4	0	~9	NaOH	0.4	0	No	Stable
~9	0.4	0	~9	NaOH	0.4	0	No	Stable
~9	0.1	0	~9	NH$_4$OH	0	0	Yes	Coagulated
~9	0.3	0	~9	NH$_4$OH	0	0	Yes	Coagulated
~9	0.4	0	~9	NH$_4$OH	0	0	Yes	Stable
~9	0.4	0	2.0	—	0	0	No	Coagulated
~9	0.4	0	2.0	—	0	0	Yes	Coagulated

[a] Stabilizer level, based on the weight of calcium carbonate solids in the PCC slurry; solids content of the P(BMA/BA) latex used was ~38%; solids content of PCC was 14.4%; the designed wt % of PCC particles in each PCC/P(BMA/BA) latex blend (based on solids) was 35%.
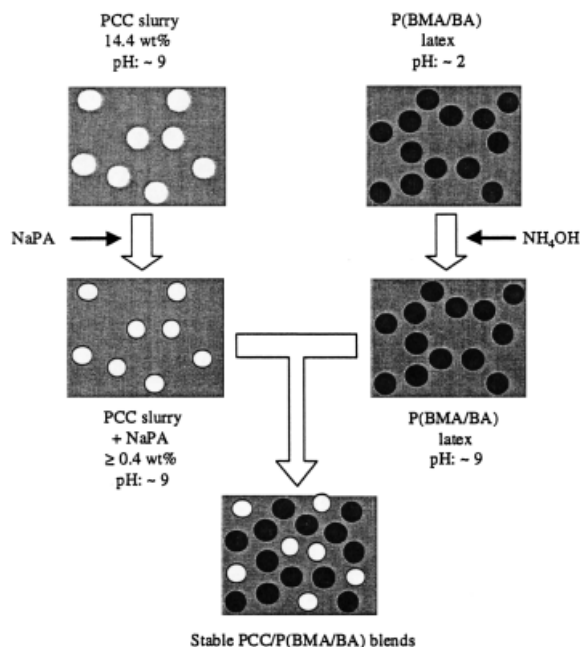
Figure 2 Schematic diagram of the procedure used to prepare stable PCC/P(BMA/BA) blends; each mixture was held for 20 min after each step in this process.

pared by simply mixing two or more polymer latexes, the blend of PCC with P(BMA/BA) latex synthesized by the method published elsewhere[8] always coagulated when they were simply mixed. Altering the surface characteristics of the P(BMA/BA) latex particles by increasing the pH, adding surfactant (SDS), or introducing carboxyl groups on the surface of the P(BMA/BA) latex particles failed to solve this problem. Table II summarizes some of the results of a formulation study to prepare stable PCC/P(BMA/BA) blends. It was observed from Table II that only when NaPA (sodium polyacrylate; MW = 5100 g/mol; Aldrich) stabilizer was added to the PCC could a stable PCC/P(BMA/BA) blend be obtained. It could be concluded that regardless of the carboxyl group content or the extent of neutralization of the carboxyl groups present on the latex, a polymer stabilizer (e.g., NaPA) added to the PCC component is needed to obtain a stable PCC/P(BMA/BA) blend. The minimum NaPA level in the PCC slurry that was required to prepare a stable PCC/P(BMA/BA) blend is 0.4 wt % (based on the weight of the calcium carbonate solids). The successful procedure used to prepare stable PCC/P(BMA/BA) blends is illustrated in Figure 2.

It appears that the addition of a stabilizer such as NaPA is essential, and the adjustment of pH is also important to obtain stable PCC/P(BMA/BA) blends. This necessitated a detailed examination of the mechanism by which stability was achieved in the blend.

Mechanism for the stability of the blend of precipitated calcium carbonate and P(BMA/BA) latex

Latex particles may be colloidally stable due to the presence of charges on the particle surface (negative or positive; electrostatic stability). A repulsive force between particles results from the same surface charge. To understand the mechanism of the stability of PCC particles during the blending process with P(BMA/BA) or during the addition of NaPA, an investigation of the surface charge on the PCC particles needed to be carried out.
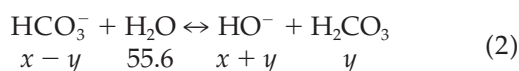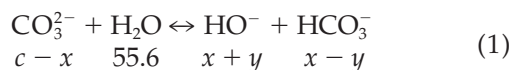
Surface charge of PCC particles in the absence of NaPA stabilizer

As mentioned above, the surface charge of particles is very important for colloidal stability. To study the mechanism of stability of PCC particles when blended with P(BMA/BA) latex, the surface charge of the PCC particles was examined first. Two methods were utilized to estimate the surface charge of the PCC particles as described below.

Theoretical prediction of the surface charge of PCC particles

The surface of an inorganic pigment (e.g., calcium carbonate) by itself possesses a surface charge in water that provides some degree of electrostatic stability. The surface charge is characteristic of the pigment itself and the pH of the aqueous media surrounding the pigment. In this regard, each pigment has an isoelectric point corresponding to the pH where the negative and positive charges on the pigment surface just neutralize each other. As the pH is adjusted away from this isoelectric pH, a charge imbalance starts to develop that leads to pigment particle repulsion. The sign of the charge on the particle surfaces may be determined based on the isoelectric point and the pH of the aqueous phase. Calcium carbonate crystals have an isoelectric pH of 9.6 in water.[13] For the PCC slurry at room temperature, the equilibrium pH value is determined by the solubility of calcium carbonate in water and its hydration constant. If the equilibrium pH of the PCC slurry is lower than the isoelectric pH of the calcium carbonate crystal, the surface charge present on the PCC pigment particle surface is positive, equal to the isoelectric pH, zero, or negative otherwise. The equilibrium pH value can be calculated according to the hydration equation of calcium carbonate, and can also be measured.

In the PCC slurry, calcium carbonate is slightly soluble in the aqueous medium. The hydration of PCC can be expressed as in eqs. (1) and (2).

$$CO_3^{2-} + H_2O \leftrightarrow HO^- + HCO_3^-$$
$$c - x \quad 55.6 \quad x + y \quad x - y \tag{1}$$

$$HCO_3^- + H_2O \leftrightarrow HO^- + H_2CO_3$$
$$x - y \quad 55.6 \quad x + y \quad y \tag{2}$$

where c is the solubility of calcium carbonate in water at room temperature (M), x is the reduction of the concentration of the CO_3^{2-} ion due to hydration (M), y is the concentration of carbonic acid (M), and $x+y$ (=[OH]) is the concentration of hydroxyl groups (M), which determines the pH. From eqs. (1) and (2) and the dissociation reactions of carbonic acid, eqs. (3) and (4) can be obtained.

$$\frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} = \frac{10^{-14}}{k_2} \tag{3}$$

$$\frac{[OH^-][H_2CO_3]}{[HCO_3^-]} = \frac{10^{-14}}{k_1} \tag{4}$$

where k_1 and k_2 are the first and second dissociation constants of carbonic acid in water at room temperature, respectively.

If the influence of atmospheric carbon dioxide on the pH of this system is ignored, the concentration of each component in this system can be assigned as illustrated in eqs. (1) and (2), and calculated using eqs. (3) and (4). This calculation resulted in the following solutions, choosing $c = 1.40 \times 10^{-4}$ M, $k_1 = 4.30 \times 10^{-7}$ M, and $k_2 = 5.61 \times 10^{-11}$ M:[14]

$$[OH] = 9.228 \times 10^{-5} M \quad pH = 9.97$$

$$[H_2CO_3] = 2.3 \times 10^{-8} M$$

The calculated concentration of H_2CO_3 is much lower than the solubility of carbon dioxide in water at room temperature, which means that the influence of atmospheric carbon dioxide cannot be neglected. Thus, the concentration of carbon dioxide in water equilibrated with the partial pressure of the carbon dioxide in the atmosphere should be chosen as the approximate concentration of H_2CO_3 in the serum of the PCC slurry, which is 9.89×10^{-6} M.[14] Thus, the equilibrium concentration of CO_3^{2-} becomes c-[OH]. Reapplying eqs. (3) and (4), the following solutions are obtained:

$$[OH] = 7.66 \times 10^{-6} M \quad pH = 8.88$$

The calculated equilibrium pH value of the PCC slurry (8.88) is lower than the isoelectric pH of calcium carbonate (pH = 9.6), which indicates that the surface charge of the PCC pigment particles is positive if there is no stabilizer present.
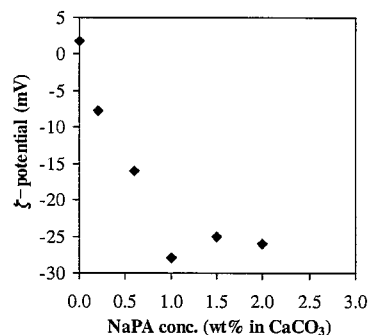

Figure 3 ζ-Potential of the PCC pigment particles dispersed in water at room temperature: pH ~9.

Experimental measurement of the surface charge of PCC particles

Besides determining the sign of the surface charge of the PCC pigment particles in their slurry form using the theoretical calculations, the surface charge can also be estimated using ζ-potential measurements. The surface charge determines the mobility of the pigment particles in an applied electrical field. A parameter that can be deduced from the electrophoretic mobility is the ζ-potential of a particle, which is the electrical potential at the edge of the shear plane around the particle. The ζ-potential can be used as a relative measure of the stability of the particles. It can be negative or positive depending on the nature of the charge on the particles. Figure 3 shows the ζ-potential of the PCC pigment particles dispersed in water. The data shows that the ζ-potential is close to zero, but positive, if there is no adsorbed NaPA present on the PCC particles, indicating that the surface charge of the PCC pigment particles is slightly positive. The experimental results are consistent with the theoretical calculations.

Influence of NaPA on the surface charge of PCC particles

ζ-Potential vs. the Concentration of NaPA Stabilizer

Further experiments investigated the change of the ζ-potential with the change of the concentration of the NaPA (expressed as the wt % of NaPA, based on the weight of calcium carbonate solids in the PCC slurry) (Fig. 3). It is found that the NaPA not only changed the sign of the ζ-potential, but also made the ζ-potential more negative as the concentration of NaPA increased further. The data shown in Figure 3 indicate that the minimum ζ-potential would occur at around 1 wt % NaPA. When there is no NaPA present in the PCC slurry, the PCC pigment particles adsorb the Ca^{2+} provided by the dissociation of dissolved calcium carbonate and make the particles positively charged.[15] The mechanism by which the added NaPA changes
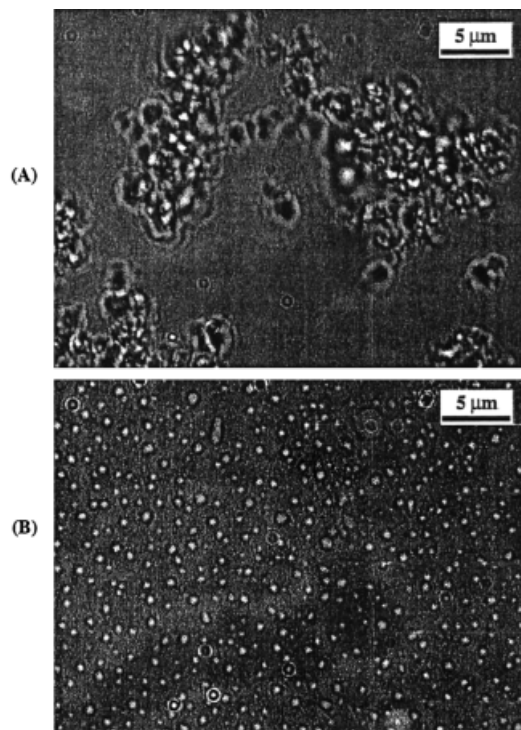
Figure 4 Optical microscope images of the wet PCC pigment particles (in slurry form): (A) without any NaPA present; (B) with 2 wt % NaPA (based on calcium carbonate solid) present.

the sign of the surface charge of the PCC pigment particles may be that NaPA molecules are adsorbed on the surface of the PCC pigment particles and the carboxyl groups on the NaPA molecule associate with the Ca^{2+} ions, which first neutralizes the positive changes and then results in a negatively charged surface. As the concentration of NaPA increases, the number of molecules of NaPA per unit surface area increases, which results in an increase in the density of the negative surface charge. The minimum point in the ζ-potential might be determined by the saturation adsorption of NaPA molecules on the surface of the PCC pigment particles and/or the concentration of the NaPA in the aqueous phase (see the following section for details).

Enhancement of PCC particle stability by the presence of NaPA stabilizer

The enhancement in stability of the PCC particles in the presence of NaPA can also be observed directly using an optical microscope. Figure 4 shows two typical images of the PCC slurries with and without NaPA stabilizer present. The micrographs show that the PCC pigment particles are not stable on a microscale if there is no stabilizer present, although the dispersion looks stable by eye [Fig. 4(A)]. Large clus-

ters of the PCC pigment particles are obviously present in Figure 4(A). However, when 2 wt % NaPA was added to the PCC slurry, the dimension of the clusters was substantially decreased, showing a enhanced stability of the PCC pigment particles in the presence of NaPA.

For latex particles stabilized by anionic surfactant [such as P(BMA/BA) stabilized by SDS], the particles adsorb the SDS molecules giving the surface a negative charge, resulting in a negative ζ-potential. However, PCC pigment particles have a positive ζ-potential when dispersed in water if there is no stabilizer present. It is these opposing charges that caused the immediate flocculation of the blends when the PCC slurry was simply blended with P(BMA/BA) latex. Knowing this, two strategies could be used to solve this problem: one is to change the negative charge of the P(BMA/BA) latex to a positive one, and the other is to change the charge of the PCC particles from positive to negative before blending. For the system investigated, the second strategy seemed more feasible. When NaPA is added in the PCC slurry, the NaPA adsorbed onto the surface of the PCC particles, thereby making it negatively charged. The ζ-potential of the PCC particles then had the same sign as the P(BMA/BA) latex particles. This resulted in repulsion between the latex particles and the PCC pigment particles and a stable blend was formed. However, as shown in Table II the addition of SDS into the PCC slurry did not help in preparing a stable PCC/P(BMA/BA) blend. This could be explained by the following possibilities: (1) the physical adsorption of SDS on the PCC particle surface is weak; (2) the association strength of the sulfate groups with the Ca^{2+} ions is not as strong as that of the carboxyl groups with the Ca^{2+}; (3) a SDS molecule has only one sulfate group, which cannot bring free sulfate group to the PCC particle surface if the SDS molecule is adsorbed on the surface through the sulfate group/Ca^{2+} association. The poor efficiency of SDS in enhancing the stability of the PCC slurry might result from one, two, or three of the above factors.

Stabilizer (NaPA) behavior

To further study the adsorption of NaPA on PCC pigment particles, the conductance of a PCC slurry containing NaPA was measured as a function of added NaPA concentration (Fig. 5). The results show that the conductance was initially constant as the NaPA concentration increased until reaching a transition point (0.12 wt % NaPA in the aqueous phase). This suggests that all the NaPA molecules were adsorbed on the PCC particles before this point. This indicates that the adsorption of NaPA on the surface of the PCC particles is strong. When the NaPA con-

centration reached this transition point, all of the PCC particles were covered with NaPA (saturated), and they could no longer adsorb additional NaPA molecules. At this point, NaPA reached a saturation adsorption on the PCC particles. All of the NaPA added after this transition point went into the aqueous phase instead of being adsorbed on the surface of the PCC particles. Thus, the conductance increased linearly as the concentration of NaPA increased after this point. Based on the concentration of NaPA at the saturation point and the average PCC particle size of 100 nm, the surface area covered by each NaPA molecule was calculated as being 2500 Å^2/molecule. The concentration of NaPA (expressed as wt % based on the weight of the aqueous phase) in the serum of the PCC slurry at the saturation adsorption point (0.12 wt %) is equivalent to a NaPA stabilizer level of 0.71 wt % (expressed as wt % based on the weight of calcium carbonate solids). This concentration is lower than the point where the minimum ζ-potential is reached as shown in Figure 3. This shows that both the saturation adsorption of the NaPA molecules on the surface of the PCC pigment particles and the concentration of NaPA in the aqueous phase determine the minimum ζ-potential of these pigment particles.

Surface properties of precipitated calcium carbonate/latex blend films

Influence of carboxyl group coverage on the latex particles on the gloss and surface morphology: effect on gloss

Gloss was measured on glass microslide substrates at 75° incident angles. Results presented in Figure 6 show that as the concentration of the carboxyl groups on the P(BMA/BA) latex particles increased, there was a corresponding increase in gloss. In the PCC/P(BMA/BA) blend films, gloss is expected to increase
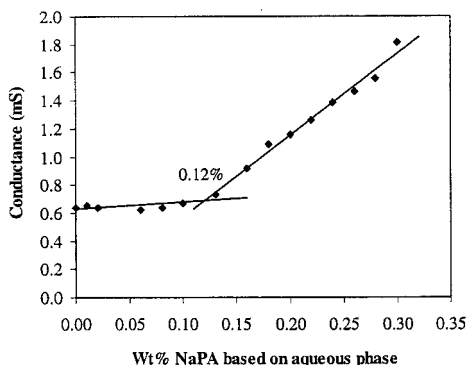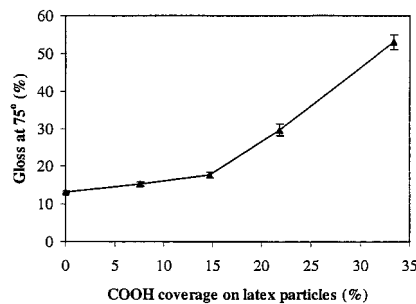
Figure 6 Surface gloss of PCC/P(BMA/BA) latex blend films as a function of the carboxyl coverage on the surface of the P(BMA/BA) latexes; vol % PCC = 17%; glass microslide substrate; 3-mil draw-down bar used.

with: (1) an increase in the gloss of the copolymer matrix; (2) an increase in the specular angle at which the measurement is made; and (3) an increase in the microscopic surface smoothness. When the specular angle is fixed at 75°, as in this work, the gloss only depends on the refractive index and the surface microsmoothness. To determine which parameter contributes to the increase in the gloss as the carboxyl group coverage on P(BMA/BA) latex particles was increased, parallel experiments were performed using a pure P(BMA/BA) latex film. In the series of experiments using pure P(BMA/BA) latex films, the carboxyl group coverage on the P(BMA/BA) latex particles was changed to the same extent as in the PCC/P(BMA/BA) blend system (from 0 to 33%, Fig. 7). Figure 7 shows that the gloss of the pure P(BMA/BA) latex films increased with an increase in the carboxyl group coverage on the P(BMA/BA) latex particles, although the overall extent of the increase was low (increase ~50%). These results indicate that the presence of the carboxyl groups on the P(BMA/BA) latex particles increases the gloss of the PCC/P(BMA/BA) blend film through an increase in the gloss of the copolymer matrix.

Further comparison between the results of the parallel experiments and the results presented in Figure 6 show that the overall extent of the increase
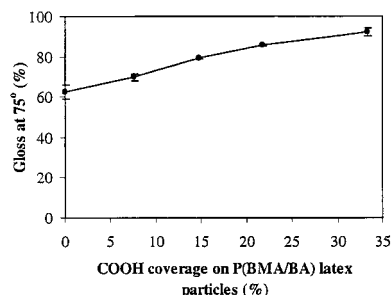
Figure 5 Conductance of a PCC slurry as a function of NaPA concentration (NaPA saturation point: 0.12%); solids of the PCC slurry = 14.4%; room temperature; pH ~9.0.

Figure 7 Gloss vs. carboxyl group coverage on the pure P(BMA/BA) latex particles; glass microslide substrate; 3-mil draw-down bar used; $D_{n,P(BMA/BA)}$ ~125 nm.
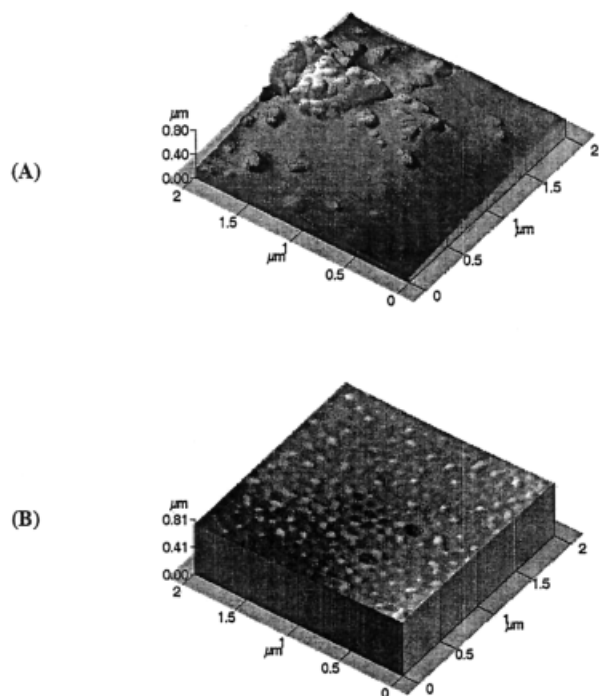
Figure 8 AFM topographical images of films cast from PCC/P(BMA/BA) blends: (A) without carboxyl groups present on the P(BMA/BA) latex particles; (B) with 33.3% carboxyl group coverage on the P(BMA/BA) particles; vol % of PCC = 17%; glass microslide substrate; 3-mil draw-down bar used.

in the gloss of PCC/P(BMA/BA) blend films (over 300%) is much more significant than that of the pure P(BMA/BA) latex films (only ~50%). This comparison implies that there might be another factor, other than the contribution from the copolymer matrix, that also accounts for the increase in gloss of the pigmented latex films as the carboxyl coverage on the soft particles increases. It should be noted, however, that the absolute value of gloss for the PCC/P(BMA/BA) blend film is lower than the pure P(BMA/BA) latex films or the PS/P(BMA/BA) latex blend films at all of the carboxyl group coverages that were examined.

Effect on surface morphology

Based on the work published previously,[12] the microscopic surface smoothness significantly influences the gloss of latex blend films. Atomic force microscope (AFM) observations of the surface of the PCC/P(BMA/BA) blend films show that the presence of the carboxyl groups on the P(BMA/BA) latex particles substantially changed the surface smoothness of the pigmented latex films (Fig. 8). As Figure 8 shows, there are large clusters of PCC particles present on the surface of the PCC/noncarboxylated P(BMA/BA)

blend film, resulting in a very rough surface [Fig. 8(A)], while no clusters were formed on the surface of the PCC/carboxylated P(BMA/BA) blend film [Fig. 8(B)]. Thus, the distribution of PCC particles in the PCC/carboxylated P(BMA/BA) blend film is much more uniform than that in the PCC/noncarboxylated P(BMA/BA) blend film and the surface smoothness is much higher. When PCC particles are blended with carboxylated P(BMA/BA) latex particles, the calcium carbonate on the PCC surface may react with the carboxyl groups present on the P(BMA/BA) particles. This acid-base reaction may increase the wetting ability of P(BMA/BA) polymer on the PCC particle surface.[16,17] The increased wettability of P(BMA/BA) polymer aids in the deposition of the P(BMA/BA) latex particles on the surface of the PCC pigment particles during the film formation process. This deposition prevents the clustering of the PCC particles, yielding a uniform distribution of PCC particles within the P(BMA/BA) copolymer matrix and results in the formation of a pigmented latex film with a smooth surface. Thus, the presence of the carboxyl groups on the P(BMA/BA) latex particles increases the gloss of the PCC/P(BMA/BA) blend films through the increase of the gloss of the copolymer matrix and the improvement of the uniformity of the PCC particles within the copolymer matrix.

Influence of the composition of the PCC/ P(BMA/BA) blends on gloss

PCC is a chalky white pigment that has a relatively high density (2.68 g/cm^3) and is used for high and low gloss paper coatings. The particles are negatively charged when stabilized with NaPA. It was found that the gloss was reduced with an increase in the PCC concentration in the PCC/P(BMA/BA) latex blends (Fig. 9). As explained earlier, gloss is a surface property that is dependent on the smoothness of the surface on a microscale. The greater the concentration of the PCC present, the greater the number and dimen-
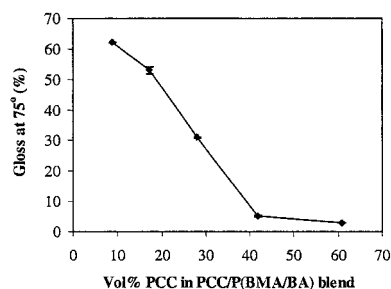

Figure 9 Gloss vs. PCC concentration in PCC/P(BMA/BA) latex blends; glass microslide substrate; 3-mil draw-down bar used; carboxyl group coverage on latex particles = 33.3%.

sions of particle clusters that are formed. The formation of these clusters leads to increased roughness on the surface of the film, which results in reduced gloss. Thus, as the PCC concentration was increased, the gloss of the pigmented P(BMA/BA) latex films gradually decreased, before reaching a concentration of 42 vol % PCC in the PCC/P(BMA/BA) blend films. At 42 vol % of PCC, the gloss vs. PCC vol % curve suddenly leveled off at a very low gloss value. Further increases in the PCC vol % did not affect the gloss significantly in the range examined. This is the point at which the critical pigment volume concentration (CPVC) for this system was reached.[18,19] The CPVC value obtained is 42 vol %.

Several methods can be used to measure the CPVC value of the PCC/P(BMA/BA) blend system. In this work, the CPVC was also determined by monitoring the change in transparency of the films as the vol % of the PCC pigment particles in the PCC/P(BMA/BA) blends was increased (Fig. 10). Figure 10 confirms that the same CPVC value was obtained for this system.

Influence of the film thickness on gloss

Results show that regardless of the volume fraction of the PCC particles in the PCC/P(BMA/BA) blend films, the gloss is higher for thicker films (Fig. 11). The explanation for this result is the effect of the substrate on gloss. Because the surface of the black plastic substrate is not smooth on a microscale, the film layer that is in contact with the substrate takes on the shape of the surface. In the case when the film is thick enough, the shape of the substrate will not affect the uppermost layer of the film, and gloss will therefore not be affected. This suggests that a threshold thickness will be attained whereby gloss will cease to increase with thickness.

CONCLUSIONS

Stable PCC/P(BMA/BA) latex blends can be prepared using NaPA as the stabilizer. The addition of NaPA to
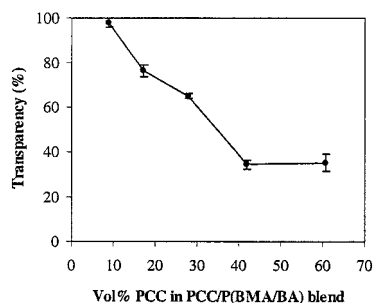

Figure 10 Transparency vs. PCC concentration in PCC/ P(BMA/BA) latex blends; glass microslide substrate; 3-mil draw-down bar used; carboxyl group coverage on P(BMA/ BA) binder latex particles = 33.3%.
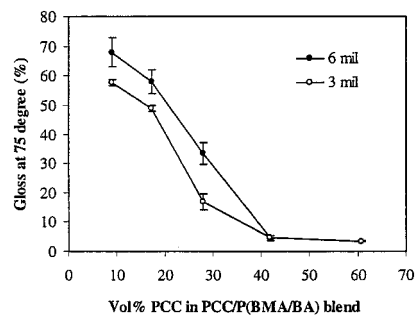

Figure 11 Gloss measured at a 75° incident angle vs. the vol % of PCC pigment particles in the PCC/P(BMA/BA) blend films having two different initial wet film thicknesses with the same solids content (25 wt %); on Leneta plastic substrate; carboxyl group coverage on P(BMA/BA) binder particles = 33.3%.

the PCC slurry changes the ζ-potential of the PCC particles from positive to negative, the same sign of the charge as the P(BMA/BA) latex particles, which is the reason why a stable PCC/P(BMA/BA) latex blend can be obtained.

The surface characteristics of the PCC and P(BMA/ BA) latex particles significantly influence the surface properties of films prepared from blends of the PCC pigment and P(BMA/BA) latex. The presence of carboxyl groups on the P(BMA/BA) latex particles improves the gloss of the PCC/P(BMA/BA) latex blend films. The composition of the PCC/P(BMA/BA) latex blends also strongly influences the gloss of the resulting films. An increase in the PCC concentration in the PCC/P(BMA/BA) latex blends results in a decrease in the gloss of the films by increasing the dimensions and concentration of the PCC clusters present on the surface of the film. It was also found that a thicker film resulted in higher gloss value.

The presence of carboxyl groups on the P(BMA/ BA) latex particles significantly improves the uniformity of the distribution of the PCC particles within the P(BMA/BA) copolymer matrix and the gloss of the resulting films. This phenomenon could be explained by the acid-base reaction between the calcium carbonate on the surface of the PCC particles and the carboxyl groups present on the carboxylated P(BMA/ BA) latex particles. This acid-base reaction improves the wetting ability of the P(BMA/BA) copolymer on the surface of the PCC particles and makes the binder particles coagulate and become deposited on the surface of the PCC particles. The P(BMA/BA)-coated PCC pigment particles could not form clusters of the PCC particles, which results in a uniform distribution of the PCC pigment particles within the P(BMA/BA) copolymer matrix and good gloss for the PCC/ P(BMA/BA) blend films.

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