

Surface Treatment and Characterization of Functionalized Latex Particles and Inorganic Pigment Particles Used in the Study of Film Formation from Pigmented Latex Systems

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ABSTRACT: The adsorption of sodium polyacrylate [NaPA] on noncarboxylated and carboxylated poly(*n*-butyl methacrylate-*co*-*n*-butyl acrylate) [P(BMA/BA)] latexes and ground calcium carbonate (GCC) was studied. The adsorption isotherms of NaPA on P(BMA/BA) latex surfaces showed that NaPA tended to adsorb to a greater extent onto the latex particle surfaces when the carboxyl group surface coverage of latex polymer particles is low, which indicates a repulsive interaction between the dissociated carboxyl groups and NaPA macroions. The electrophoretic mobility of cleaned model P(BMA/BA) latexes decreased with the increasing carboxyl group surface coverage at pH 10 due to the alkali-swelling characteristics of carboxylated latexes.

For GCC, used as extender pigment particles in the pigmented latex blend systems, the size of the GCC pigment particles stabilized with NaPA decreased during a sonification process and their ζ -potential became increasingly negative with the addition of NaPA to the GCC pigment slurry. Particle size and ζ -potential measurements showed that NaPA can stabilize GCC particles effectively, and the optimum concentration of NaPA to stabilize GCC is around 1 wt % based on solid GCC. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 398–404, 2006

Key words: adsorption; functionalization of polymers; surface characterization

INTRODUCTION

Most latex coatings and paints are, in practice, pigment (extender)/polymer latex (binder) blends. The purpose of the latex is to bind pigment particles to each other and to bond them to the substrate onto which the coating is applied after the latex forms a continuous film upon drying. Binder polymers can also significantly influence the rheology, coater runnability, drying behavior of the coating formulations, and the optical and viscoelastic properties of the coating products.¹ Extender pigments are another major component in a surface coating system. The extender pigments are available in a granular or powder form, and are practically insoluble in the application medium.² They are used in coating formulations to modify or influence certain physical properties; for instance, in paper coating products, the main reason for using extender pigments, such as calcium carbonate, is to improve the optical properties of the coatings in terms of brightness and opacity.³ In a typical pigment/polymer latex blend system, the soft latex particles deform during the film formation process in a manner similar

to the frequently described “four-stage” film formation model.^{4,5} It can be envisioned that the hard particles, that is, the pigment particles, will not deform during the latex film formation process and will retain their original shapes and serve as a reinforcing filler for the coalesced soft polymer matrix.

For such surface coating systems, many fundamental questions remain unanswered. For example, during the film formation process, differences in the surface properties of the latex binder and pigment particles can lead to various types of interactions (e.g., synergistic or antagonistic) between these two components. These interactions will in turn affect the distribution of the pigment particles within the soft matrix formed by the deformed latex particles in the resulting films. Film morphologies, drying kinetics, and mechanical and surface properties of the films will also be influenced by these interactions. In this work, the influence of the latex and pigment particle surface characteristics on the film formation process from pigmented latex systems will be studied.

Stabilizers are also a very important component in coating formulations other than the binder and extender particles. It is a general rule that: (a) the more ionic the surfactant and (b) the greater the affinity of its adsorbed ion for the pigment particles, the more effective is the surfactant dispersive action. Among the materials ideally equipped to impart this type of

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ionic activity are the polyelectrolytes.⁶ A polyelectrolyte is a macromolecule built up partly or entirely from monomeric units with ionizable groups. It is characterized by a backbone macroion (a single large ion possessing a number of similarly charged groups connected by chemical bonds) and an equivalent number of small, independent, and oppositely-charged balancing ions (counterions).⁶

The polyelectrolytes can adsorb at a solid/solution interface to provide a boundary layer that prevents close particle approach. Stabilization of pigment and polymer dispersions occurs both by electrostatic repulsion between similar charges and by steric hindrance (development of a solvation sheath enveloping the particles). Both stabilizing mechanisms are always present to some extent.⁶ Therefore, it is important to quantify the amount of adsorbed polyelectrolyte on both latex binder and extender particles in the formulation. Also, when charges are present in a macromolecular solution near a surface onto which the polymer will adsorb, several features that do not play a role in uncharged systems show up. If the polymer is charged, the mutual repulsion between the polymer chain segments opposes the accumulation of polymer chains in the surface region. If, in addition, the surface carries a charge, there is an electrostatic contribution to the segment-surface interaction that either promotes or counteracts the adsorption of polymer, depending on the sign of the charges. The general effect of a surface charge is that the surface charge has to be compensated by counterions in the double layer, which compete for space with the uncharged segments. Fler et al.⁷ have pointed out that when the polymer and surface have the same sign of charge, the main factors affecting the polymer adsorption are the segment-segment repulsion and segment-surface repulsion.

Calcium carbonate (CaCO_3) is a broadly used commercial pigment in paper coatings and house paints. As an extender pigment, it can efficiently cover the substrate and lead to shorter drying times and a lower cost. Acrylic latex polymers and copolymers are extensively used as polymeric binders in coatings and paints due to their flexible film formation temperatures and good elasticity and weatherability in the resulting films. It has been reported that calcium carbonate pigment slurries could be stabilized with sodium polyacrylate (NaPA).^{3,8,9} Therefore, the specific model system that was used in this film formation study is a blend of GCC pigment and P(BMA/BA) (both noncarboxylated and carboxylated) lattices, with NaPA employed as the stabilizer.

In this article, the adsorption of NaPA on the surfaces of functionalized P(BMA/BA) latex and GCC pigment particles was studied. Adsorption isotherms of NaPA on P(BMA/BA) latexes were determined at room temperature. Electrophoretic mobility (zeta po-

tential) of cleaned latex and uncleaned GCC particles was measured. The effect of the amount of NaPA on GCC particle size and zeta potential was also investigated.

EXPERIMENTAL

Materials

n-Butyl methacrylate (BMA), *n*-butyl acrylate (BA), and methacrylic acid (MAA) monomers (Sigma-Aldrich, Milwaukee, WI; reagent grade) were purified by passing them through columns filled with an appropriate inhibitor-removal packing material (Sigma-Aldrich, Somerville, NJ). Sodium lauryl sulfate (SLS; Fisher Scientific, Fair Lawn, NJ; reagent grade) and potassium persulfate (KPS; Fisher Scientific, Fair Lawn, NJ; reagent grade) were used as received without further purification. A cationic ion-exchange resin (20–50-mesh; AG 50W-X4, Bio-Rad Co., Hercules, CA) and an anionic ion-exchange resin (20–50-mesh; AG 1-X4, Bio-Rad Co., Hercules, CA) were cleaned following the method suggested by van den Hul and Vanderhoff.¹⁰ Sodium hydroxide (NaOH, Fisher Scientific, Fair Lawn, NJ; reagent grade), sodium polyacrylate (NaPA, molecular weight (MW) = 5100 g/mol, Aldrich, Milwaukee, WI), and ultrafine ground calcium carbonate (GCC, Covercarb® HP, Omya, Proctor, VT; particle size = 650 nm with a broad size distribution) were used as received.

Latex synthesis and basic characterization

Monodisperse latex particles with varying particle size, varying degrees of carboxylation, and controlled glass transition temperatures (T_g) were prepared via a well-designed semicontinuous emulsion copolymerization procedure. The appropriate comonomer feeding rates can be adjusted to control both the uniformity in particle size and copolymer composition based on a theoretical calculation.¹¹ The emulsion polymerization details are described elsewhere.¹² The density of surface functional groups on the latex particles was quantified by time-dependent conductometric titration experiments developed by Nishida et al.¹³ The time-dependent titration results revealed that the carboxyl group surface coverage varied from 0 to 100% as the MAA amount increased from 0 to 10 wt %, based on BMA/BA comonomer, during the semicontinuous polymerization process. Table I lists the basic characterization results of model P(BMA/BA) latex particles with a particle size about 250 nm in diameter.

Cleaning of latexes

The latexes were cleaned with an ion-exchange method before they were characterized.¹⁴ This method

TABLE I
Characterization Results of Model P(BMA/BA) Latex Particles Used in the Study of Film Formation from Pigmented Latex Systems

Sample	1	2	3	4	5
D_w^a (nm)	243.8	251.9	247.1	240.1	259.3
D_n^b (nm)	239.6	238.8	225.6	231.9	254.7
PDI ^c	1.02	1.06	1.09	1.04	1.02
Wt % of MAA ^d	0	1	3	6	10
—COOH surface coverage (%) ^e	0	9.8	23.1	56.4	100
T_g (K)	272.3	271.8	273.5	274.0	272.9

^a D_w = weight-average particle diameter.

^b D_n = number-average particle diameter.

^c PDI = polydispersity index ($= D_w/D_n$).

^d Based on the weight of the (BMA/BA) comonomer used during the semi-continuous emulsion copolymerization process.

^e The cross-sectional area of each carboxyl group is 20 \AA^2 .²⁰

uses analytical-grade anionic and cationic ion-exchange resins (Bio-Rad). The cationic ion-exchange resin was extensively washed with deionized (DI) water before use. The anionic ion-exchange resin was converted from its chloride form into its hydroxide form with a 3N aqueous sodium hydroxide solution followed by complete washing with DI water. The two cleaned resins were mixed in a weight ratio of 51 : 49 AG 50W-X4/AG 1-X8 just before use. Latex samples were diluted to approximately a 5% solids content. The ratio of the solid polymer to the mixed resins was 1 : 1, and the mixture was agitated with magnetic stirring or mechanical stirring for 2 h for each cleaning cycle. The conductance of the latex was measured after each ion-exchange cycle. This ion-exchange procedure was repeated until the conductance of the latex reached a constant value close to that of deionized water. This procedure usually required four cycles.

Surface treatment and characterization of latexes and pigment particles

The adsorption behavior of NaPA on the latex particle surfaces was investigated by measuring the adsorption isotherm. The most widely used methods for obtaining the adsorption isotherm are those in which a physical separation of the stabilizer adsorbed on the latex particle surfaces and the continuous phase is made, after which the concentration of the stabilizer in the supernatant is analyzed (indirect methods). Then, the amount of adsorbed stabilizer on the latex particle surface is calculated from the difference in stabilizer concentration (before and after adsorption) in the dispersion medium (the continuous phase) of a latex-stabilizer system.

In this study, NaPA solutions of various concentrations were added to cleaned latex samples with mild stirring for ~ 12 h. Then, the serum from the latex was obtained by ultracentrifugation (L8-M Ultracentrifuge, Beckman, 30K rpm, 8 h, 4°C). The NaPA concentration in the aqueous phase was followed by conductivity,

using a YSI conductivity meter (Model 32; Yellow Springs Instrument (YSI) Co., Inc.) and a platinum immersion-type electrode (Model 3403; YSI Co., Inc.). A conductivity-concentration calibration curve was constructed at room temperature. From a mass balance calculation, the adsorption isotherms of NaPA on latex particles with different carboxyl group surface coverages were obtained.

The particle size of the GCC pigment was determined using dynamic light scattering (Nicomp Submicron Particle Sizer, Model 370, Particle Sizing Systems, Inc.) in the presence of the stabilizer, NaPA. The pigment slurry was mixed with NaPA solution after first diluting the pigment slurry using DI water. Two different mixing methods were used: (1) the diluted pigment slurry was added drop-wise into the stabilizer solution, and (2) the NaPA solution was added drop-wise into the diluted pigment slurry. In both cases, the mixture was stirred for 20 min and then sonified for 35 min at an output power of 10 and a duty cycle of 70% in a Branson sonifier (Model 450). An ice bath was used to reduce the temperature rise during the sonification process. Samples were taken during the sonification process at different times, and the particle sizes were measured using the Nicomp. The ratio of NaPA to solid pigment particles varied from 0 to 3 wt %.

The electrophoretic mobility (the zeta potential) of both pigment and latex samples were measured using the Coulter Doppler Electrophoretic Light Scattering Analyzer (DELSA 440, Coulter Company). A Coulter EMPSL 7 mobility standard (carboxyl-modified polystyrene latex particles in 0.01M sodium phosphate buffer at pH 7.0) was employed for calibrating the instrument and software.

RESULTS AND DISCUSSION

NaPA adsorption on P(BMA/BA) latex particles

The adsorption of stabilizer molecules on the latex particle surface often determines the stability of the

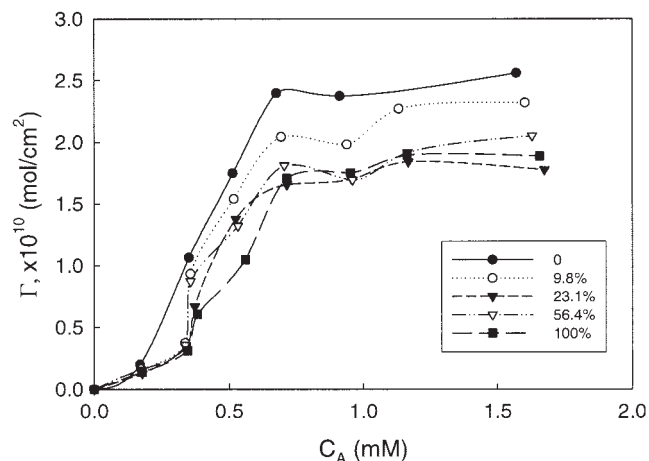


Figure 1 Adsorption isotherms of NaPA on cleaned P(BMA/BA) latex particles. Numbers in the legend represent the carboxyl group surface coverage on the latex particles; pH \sim 8; C_A : the concentration of NaPA in the aqueous phase at adsorption equilibrium; Γ : amount of NaPA adsorbed per unit surface area of latex particles.

latex. Viscosity and other colloidal properties are controlled by the addition of stabilizer to the latex systems as well. The adsorption isotherm of NaPA on P(BMA/BA) latexes is shown in Figure 1. It can be seen that when the carboxyl group surface coverage on the latex particles is small (0 and 9.8%), the adsorption of NaPA is always greater compared to the case when the carboxyl group surface coverage on the latex particles ranges from medium to full coverage (23.1%, 56.4%, and 100%). This can be explained by the fact that along with the increase in the degree of carboxylation on the latex particle surface, the repulsion between dissociated carboxyl groups and the negatively-charged NaPA macroions (i.e., the case where the charge on

the polyelectrolyte and the surface have the same sign) would become stronger at the same NaPA concentration (at pH \sim 8). Also, the amount of NaPA adsorbed on the latex particle surface remained constant (i.e., reached saturation) when the $-\text{COOH}$ surface coverage was higher than 23%. From the plateaus of the adsorption isotherms, the effective molecular area of NaPA at adsorption saturation on P(BMA/BA) can be calculated. The effective molecular area of NaPA at saturation on P(BMA/BA) is between 70 and 90 \AA^2 , depending on the amount of carboxyl groups present on the latex surface.

During the adsorption isotherm experiments, bridging flocculation was observed. For a polymeric stabilizer, such as NaPA, that is present at low concentrations, the stabilizer chains prefer to adsorb onto particle surfaces. As the stabilizer concentration increases and stabilizer molecules start to compete for latex surfaces, the backbone is forced off the surface into loops. Eventually, some ends of the stabilizer molecules are displaced and are free to adsorb onto other adjacent particles, resulting in bridging flocculation where NaPA polymer chains span two adjacent particles to form a network. To visualize this bridging flocculation phenomenon, optical micrographs of the latex samples after adsorption of NaPA are shown in Figure 2. C_A is the NaPA aqueous concentration after adsorption equilibrium was achieved in the cleaned latex systems. In Figure 2, it is shown that when the equilibrium concentration of NaPA in the aqueous phase is larger than 1.80 mM, macroscopic bridging flocculation would take place, as shown for the sample on the right in Figure 2a. Even when $C_A = 1.80$ mM, under the optical microscope, particle aggregates could be observed, as shown in Figure 2c.

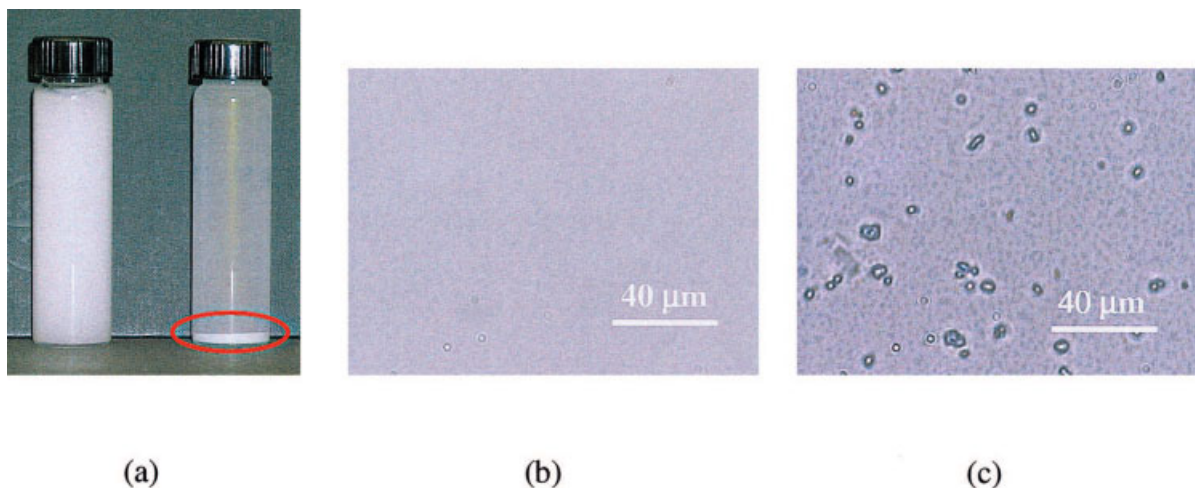


Figure 2 (a) Left vial, $C_A = 1.80$ mM; Right vial, $C_A > 1.80$ mM; (b) optical micrograph of sample with $C_A = 1.60$ mM; and (c) optical micrograph of sample with $C_A = 1.80$ mM. Surface coverage of carboxyl groups on P(BMA/BA) latexes is 56.4%; particle size = 240 nm.

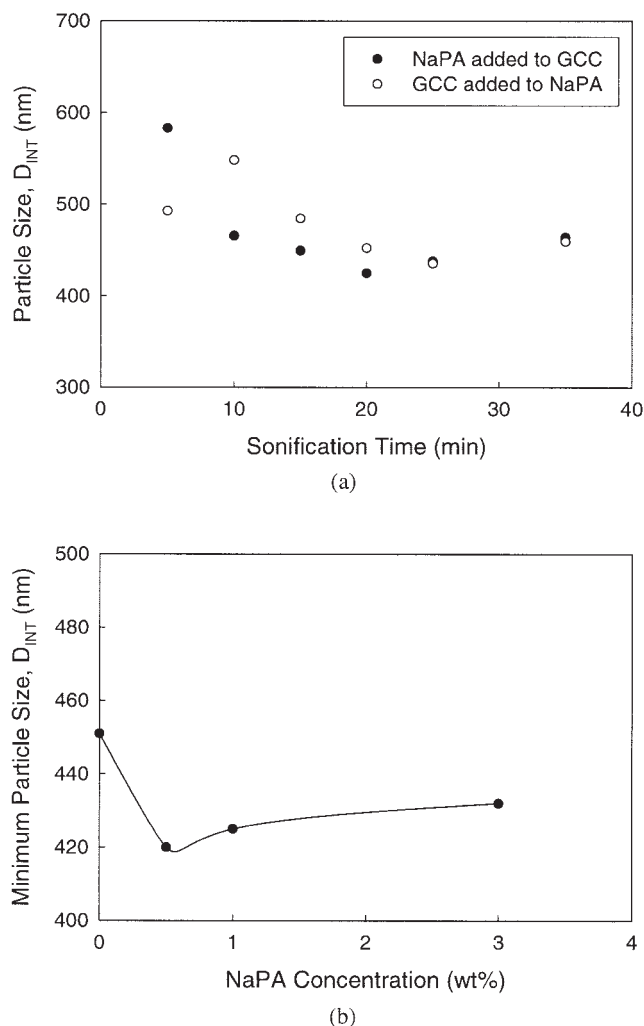


Figure 3 (a) Effect of sonification time on GCC particle size (D_{INT}) for 1% added NaPA, based on solid pigment. (Mixing methods (●) NaPA added to the GCC slurry, (○) GCC slurry added to NaPA.) (b) The effect of added NaPA to achieve a minimum GCC pigment particle size. (Mixing method: NaPA added into the GCC slurry; NaPA concentration is based on solid GCC; sonification time 20 ~ 25 min.)

NaPA adsorption on GCC pigment particles

GCC particle sizing in the presence of NaPA

As expected, the particle size of the GCC pigment in the presence of NaPA decreased during the sonification process. In this process, GCC aggregates could be broken up because of sufficient shear induced during the sonification process; a smaller particle size was obtained and more stabilizer was adsorbed on the surface of the GCC particles as a result of the increased available surface area. The smallest GCC size was obtained after 20 to 25 min of sonification. This minimum diameter was found to be around 420 nm (D_{INT} : intensity average diameter), as shown in Figure 3a. There was a small increase in the GCC particle size after the smallest particle size was obtained. The rea-

son for this is that as the particle size decreased, so did the surface coverage and the overall stability. With an increase in the total energy of shearing during the sonification process, an increase in particle size was observed, implying that some flocculation occurred after 20 min of sonification. Another noteworthy fact is that NaPA can stabilize the GCC particles, and a smaller particle size may be obtained in the presence of added amounts of NaPA, as shown in Figure 3b; however, it can also be noticed that the difference between the minimum particle size obtained from samples with additional NaPA introduced and the latex particle size obtained from samples prepared without any NaPA added is not very large. This is because the GCC pigment particles have already been stabilized by NaPA, as confirmed by the manufacturer, even though the amount of original NaPA added is not comparable to the amount that was later added into the current system. From Figure 3a, it can also be seen that the mixing sequence does not dramatically influence the GCC particle size, especially the minimum particle size.

Zeta potential measurements of pigment samples

Zeta potential is a measurable quantity that is used to approximate the particle surface potential of charged particles. It is the electrical potential between the bulk solution and the edge of the shear plane around the particle. The zeta potential can be negative or positive depending on the nature of the charge on the particles. The magnitude of the zeta potential is directly correlated to colloidal stability. In general, if the particles have low zeta potential values (for example, absolute values less than 30 mV), then the force between the particles is insufficient to prevent dispersion instability. Another reason to utilize zeta potential measurements is that for mineral products (e.g., pigment), the acid-base nature of the surface can be estimated from the isoelectric point of the surface (IEPS), which is defined as the pH of the pigment suspension in water where the surface charge is zero (i.e., the number of positive charges is equal to the number of negative charges, and the zeta potential is zero). A low IEPS value indicates an acidic surface, while a higher IEPS value indicates a basic surface. The IEPS value for calcium carbonate is 9.6,¹⁵ so that the calcium carbonate surface is basic. With latex particles whose surface is covered by a hydrophilic layer formed by acrylic acid sequences (incorporated via copolymerization or via adsorption), the interaction of latex particles and pigment particles can be explained by an acid-base interaction.¹⁶

The zeta potential value is often determined by interpreting electrokinetic measurement results. Of the electrokinetic phenomena, electrophoresis is by far the most important. Electrophoresis refers to the movement of a particle (and any material attached to

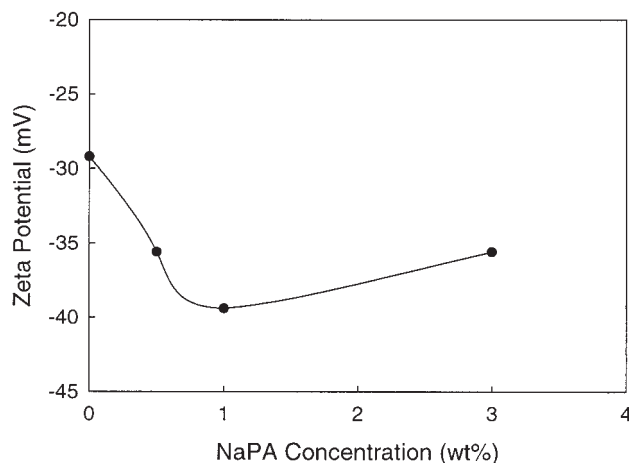


Figure 4 Zeta potential of the GCC pigment particles dispersed in water at room temperature as a function of added NaPA; pH \sim 9.

the surface of the particle) relative to a stationary liquid under the influence of an applied electric field.¹⁷ Figure 4 shows the zeta potential of the GCC pigment particles dispersed in water as a function of the NaPA concentration (expressed as wt % of NaPA, based on the weight of calcium carbonate solids in the GCC slurry) at pH 9. When there is no NaPA present in the dispersion, the zeta potential is negative, which is different from the results obtained by Huang et al.⁸ and Tang et al.,⁹ although they used different types of calcium carbonate. According to Huang et al. and Tang et al., the calcium carbonate pigment particle should be slightly positively charged in nature when there is no stabilizer present (in both cases, NaPA was used later to stabilize the pigment). The reason for this difference is that the GCC pigment slurry has been stabilized by a small amount of NaPA, which has made the surface charge of the GCC particles negative. However, from Figure 4, it is obvious that the extra addition of NaPA is able to stabilize the GCC pigment particles. As the concentration of NaPA was increased further, the zeta potential of the GCC pigment particles became more negative. This is because as the concentration of NaPA increases, more NaPA molecules will adsorb onto the GCC surface, covering the cationic active sites and giving the calcium carbonate a more anionic character. As a result, the negative potential of the GCC particles will increase. The adsorption of the polyelectrolyte (NaPA) provides the calcium carbonate particle with an electrosteric barrier, which improves the stability of the colloidal suspension. Also, the data indicate that the maximum negative value of the zeta potential would occur at around 1 wt % NaPA. This maximum value might correspond to the saturation adsorption of NaPA molecules on the surface of the GCC pigment particles.

When the stabilizer concentration increased beyond the optimum level, the zeta potential began to de-

crease from the peak value. The decrease in zeta potential with increasing electrolyte concentration is due to an effect known as electrical double layer compression. The electrical double layer can be regarded as consisting of two regions: an inner region that includes adsorbed potential-determining ions, and a diffuse region in which ions are distributed according to the influence of electrical forces and random thermal motions. The extent of the diffuse double layer around a particle is, in general, on the order of some tens of nanometers, but the exact magnitude depends on the electrolyte concentration. Increasing the electrolyte concentration causes the diffuse double layer to shrink closer to the particle, so that the electrostatic potential falls more quickly with distance.¹⁸ Since zeta potential is the electrostatic potential measured at the shear plane that is located at some fixed distance from the particle surface, it decreases as the bulk electrolyte concentration increases. From particle size measurements and determination of the zeta potential, it can be concluded that 1 wt % NaPA (based on solid GCC particles) is around the adsorption saturation point.

Electrophoretic mobility of cleaned P(BMA/BA) latex samples

The electrophoretic mobilities of cleaned latex particles (with diameters around 250 nm) at around pH 10 are shown in Figure 5 for particles with different amounts of carboxyl groups present on the particle surfaces. It can be seen that the electrophoretic mobility of P(BMA/BA) particles decreased from 5 to 1.9 μm when the carboxyl group surface coverage increased from 0 to 100% on the latex particles. Nishida previously discussed the alkali-swelling behavior of carboxylated latexes.¹⁹ As the carboxyl groups present on the latex particles were neutralized with alkali and

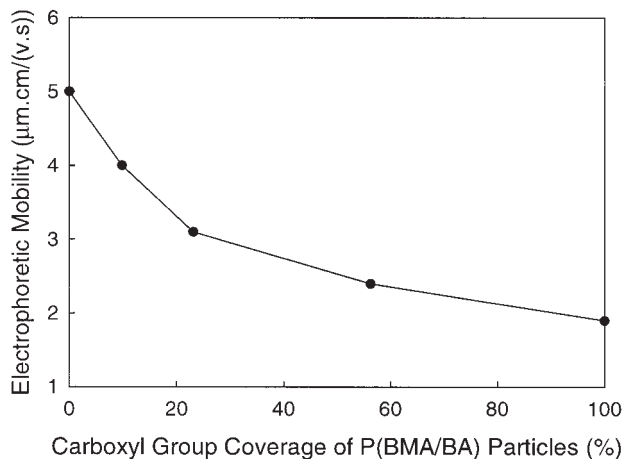


Figure 5 Electrophoretic mobility of cleaned P(BMA/BA) latex particles at pH 10; original particle diameter around 250 nm.

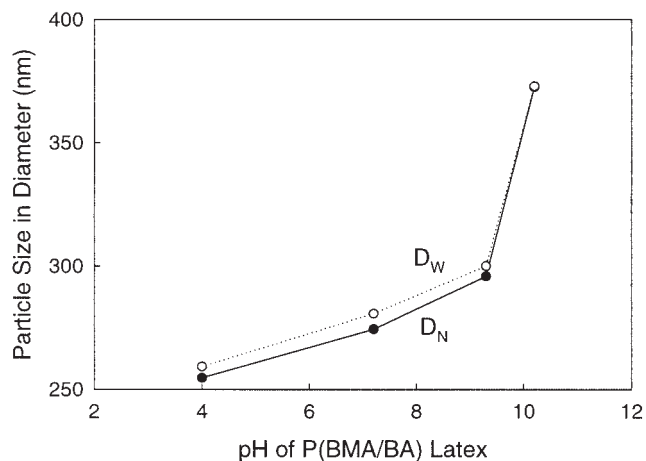


Figure 6 Particle size of cleaned P(BMA/BA) latex as a function of pH. Surface carboxyl group coverage = 100%.

their charges became increasingly negative, the charged groups became hydrated and were subject to electrostatic repulsion. As a result, the latex particles became swollen and some segments of the polymer chains began to interact with each other by hydrogen bond formation and/or chain entanglements, which caused an interaction between the latex particles. Macroscopically, this phenomenon should be reflected in changes in particle size and viscosity. In our case, the viscosity of the system won't be expected to change much because the system subjected to electrophoretic mobility measurements was extremely dilute. However, the particle size would still increase due to alkali-swelling when latex samples are carboxylated. This increase can be used to explain the changes in the electrophoretic mobility when the pH of the carboxylated latexes was high (e.g., 10). With the increase of pH, the size of the latex particles increased due to their alkali-swelling behavior. Under the same applied electric field, the velocity of the particles will decrease because the viscous drag force will increase. Therefore, the electrophoretic mobility should decrease. The electrophoretic mobility should be decreased to a greater extent with higher degrees of carboxylation because the size increase will be more significant. Figure 6 shows the particle size change as a function of pH for cleaned latex particles with 100% carboxyl group surface coverage. It can be seen that latex particle size increased as the pH of latex was increased, and this increase was greater when the pH of the latex increased from 9 to 10.

CONCLUSIONS

The adsorption isotherms of NaPA on P(BMA/BA) latex surfaces were measured and determined. NaPA tends to adsorb more strongly onto the latex particle surfaces when the carboxyl group surface coverage of latex particles is small (0 and 9.8%), which indicates a repulsive interaction between the dissociated carboxyl

groups on the particle surface and NaPA macroions. After a critical concentration of NaPA is attained, that is, 1.80 mM, aggregation of P(BMA/BA) latexes occurs as NaPA starts to link different particles together by a bridging flocculation mechanism.

The size of the GCC pigment particles in the presence of NaPA decreased during the sonification process to a minimum size of 420 nm when an optimum sonification time (20–25 min) was applied. The zeta potential of GCC particles became more negative with the addition of NaPA. Both results indicate NaPA can stabilize GCC particles. The largest negative ζ -potential and smallest particle size was attained at approximately 1 wt % of added NaPA.

From the electrophoretic mobility measurements, the cleaned model P(BMA/BA) latexes exhibited a decrease in mobility at pH 10 when higher amounts of carboxyl groups were present on the latex particle surface. The alkali swelling character of carboxylated latexes was thought to be the main reason that caused this phenomenon.

References

- Lepoutre, P.; Hiraharu, T. *J Appl Polym Sci* 1989, 37, 2077.
- Rothville, G. *Surf Coat Australia* 1996, January/February, 24.
- Engstrom, G.; Rigdahl, M. N. *Pulp & Paper Research J* 1992, 7, 90.
- Winnik, M. A. In *Emulsion Polymerization and Emulsion Polymers*; Lovelland, P. A.; El-Aasser, M. S., Eds.; John Wiley and Sons: Chichester, UK, 1997; pp 467–518.
- Voyutskii, S. S. *J Polym Sci* 1958, 32, 528.
- Patton, T. C. *Paint Flow and Pigment Dispersion: A Rheological Approach to Coating and Ink Technology*; John Wiley & Sons: New York, 1979.
- Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgroveand, T.; Vincent, B. In *Polymers at Interfaces*; Chapman & Hall: London, 1993; p 343.
- Huang, Y. C.; Sanders, N. D.; Fowkes, F. M.; Lloyd, T. B. *Coating Conf.*, Montreal, Canada, 1991; p 123.
- Tang, J.; Daniels, E. S.; Dimonie, V. L.; Klein, A.; El-Aasser, M. S. *J Appl Polym Sci* 2002, 86, 891.
- van den Hul, H. J.; Vanderhoff, J. W. *J Colloid Interface Sci* 1968, 28, 336.
- Tang, J.; Ding, T.; Daniels, E. S.; Dimonie, V. L.; Klein, A.; El-Aasser, M. S. *J Appl Polym Sci* 2003, 88, 30.
- Ding, T.; Daniels, E. S.; El-Aasser, M. S.; Klein, A. *J Appl Polym Sci*, to appear.
- Nishida, S.; El-Aasser, M. S.; Klein, A.; Vanderhoff, J. W. In *ACS Symposium Series*; Bassett, D. R.; Hamielec, A. E., Eds.; Emulsion Polymers and Emulsion Polymerization; American Chemical Society: Washington, DC, 1981; vol. 165, p 291.
- Tang, J. Ph.D. Dissertation, Lehigh University, Bethlehem, PA, 2000.
- Granier, V.; Sartre, A. *Langmuir* 1995, 11, 2179.
- Fowkes, F. M. *J Adhes Sci Technol* 1987, 1, 7.
- Hiemenz, P. C.; Rajagopalan, R. *Principles of Colloid and Surface Chemistry*; Marcel Dekker, Inc.: New York, 1997.
- Hunter, R. J. *Foundations of Colloid Science*; Oxford University Press: New York, 1987.
- Nishida, S. Ph.D. Dissertation, Lehigh University, Bethlehem, PA, 1980.
- Adamson, A. W. *Physical Chemistry of Surfaces*; John Wiley: New York, 1990.