Film Formation from Pigmented Latex Systems: Drying Kinetics and Bulk Morphologies of Ground Calcium Carbonate/Functionalized Poly(*n*-butyl methacrylate-*co-n*-butyl acrylate) Blend Films

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ABSTRACT: The drying kinetics and bulk morphology of pigmented latex films obtained from poly(*n*-butyl methacrylate-*co-n*-butyl acrylate) latex particles functionalized with carboxyl groups and ground calcium carbonate blends were studied. Latex/pigment blends with higher carboxyl group coverage on the latex particle surfaces dried faster than films with few or no carboxyl groups present. The latex/pigment dispersions also dried faster when there was more stabilizer present in the blend system because of the hydrophilic nature of the stabilizer. The net effect of increasing the pigment volume concentration in the blend system was to shorten the drying time. The bulk morphologies of the freeze-fractured surfaces of the pigmented latex films were studied with scanning electron microscopy. Scanning electron microscopy analysis showed that increased surface coverage of carboxyl groups on the latex particles in the latex/pigment blends resulted in the formation of smaller pigment aggregates with a more uniform size distribution in the blend films. In addition, the use of smaller latex particles in the blends reduced the ground calcium carbonate pigment aggregate size in the resulting films. Scanning electron microscopy analysis also showed that when the initial stabilizer coverage on the latex particles was equal to 18%, smaller aggregates of ground calcium carbonate were distributed within the copolymer matrix of the blend films in comparison with the cases for which the initial stabilizer coverage on the latex particles was 8 or 36%. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2267–2277, 2006

Key words: dyes/pigments; films; functionalization of polymers; morphology

INTRODUCTION

One important role for synthetic latexes is to serve as binders for a variety of inorganic pigments in a wide range of applications that include paints, adhesives, paper coatings, and carpet backings. In practice, the surface coating systems are often composed of pigment (extender)/polymer latex (binder) blends. Therefore, from both academic and industrial point of views, it is very important and meaningful to determine the governing parameters that control the film-formation process from pigmented latex systems.

The drying of latex films has been a longstanding interest in research. In 1973, Vanderhoff et al.[1] described the drying of latex as a three-stage process and correlated each of the stages with structural changes that occurred during film formation. From their experimental work, Croll[2] proposed a two-stage drying process for latex drying. There are also drying models concerned with lateral drying directions during the process of latex film formation. For example, Hwa[3] observed nonuniformities during the drying of a film-forming acrylic latex. In his experiments, concentric wet, flocculated, and dry regions were observed at the same time during latex drying on a glass plate. Winnik and Feng[4] reported that a film cast in a dish with vertical walls would possess a concave meniscus and would dry from the center of the film outward toward the edge. More recently, quite a few studies concerning the complex drying patterns of latex films have been published. For example, in the later stages of lateral drying, the lateral transport of both colloidal particles[5] and water[6] has been reported. Salamanca et al.[7] also conducted a systematic experimental study of the influence of lateral drying in colloidal films.

In terms of morphological studies on latex/pigment systems, a few studies have been focused on polymer/pigment interactions. For example, Sheehan et al.[8] used cryogenic scanning electron microscopy (SEM) to probe the interactions between latex particles possessing a carboxylated surface and calcium carbonate particles in a latex dispersion. They observed the deposi-

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 (nm)	243.8	251.9	247.1	240.1	259.3
D_n (nm)	239.6	238.8	225.6	231.9	254.7
Polydispersity index (D_w/D_n)	1.02	1.06	1.09	1.04	1.02
MAA (wt %)[a]	0	1	3	6	10
—COOH surface coverage (%)[b]	0.0	9.8	23.1	56.4	100
T_g (K)	272.3	271.8	273.5	274.0	272.9

[a] Based on the weight of the P(BMA/BA) copolymer.
[b] The cross-sectional area of each carboxyl group was 20 Å^2.[16]
D_w = weight-average particle diameter.
D_n = number-average particle diameter.

tion and adsorption of latex particles on the inorganic pigment surfaces. The amount of carboxylation of the latex surface influenced the extent of particle deformation and spreading. In another study, Granier and Sartre observed the ordering and adhesion of latex particles on model inorganic surfaces of calcium carbonate particles. Increasing the latex acid content enhanced the extent of particle spreading. An acid–base concept was used to explain their experimental observations.[9]

In this study, the drying kinetics and bulk morphologies of ground calcium carbonate (GCC)/functionalized poly(n-butyl methacrylate-co-n-butyl acrylate) [P(BMA/BA); carboxylated] blend films were studied to investigate the effects of the surface functionality, stabilizer amount, pigment volume concentration (PVC), and latex particle size on film formation from pigmented latex systems. A sodium salt of poly-(acrylic acid) (NaPA) dispersant was selected as the system stabilizer.

EXPERIMENTAL

Materials

n-Butyl methacrylate, n-butyl acrylate, and methacrylic acid (MAA) monomers (Sigma–Aldrich, Milwaukee, WI; reagent-grade) were purified by passage through columns filled with an appropriate inhibitor-removal packing material (Sigma–Aldrich, Somerville, NJ). Sodium lauryl sulfate (Fisher Scientific, Fair Lawn, NJ; reagent-grade) and potassium persulfate (Fisher Scientific; 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) were cleaned with the method suggested by van den Hul and Vanderhoff.[10] Sodium hydroxide (NaOH; Fisher Scientific; reagent-grade), NaPA (molecular weight = 5100 g/mol; Aldrich, Milwaukee, WI), and ultrafine 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 various particle sizes, various degrees of carboxylation, and controlled glass-transition temperatures (T_g's) were prepared via an emulsion copolymerization procedure and are reported elsewhere.[11] Noncarboxylated and carboxylated model P(BMA/BA) copolymer latexes with diameters of 150 nm were prepared with a conventional semicontinuous emulsion copolymerization process at 80°C. Larger latex particles (either 250 or 400 nm in diameter) were synthesized by a seeded emulsion polymerization process with the 150-nm latex particles as the seed. The appropriate comonomer feed rates could be determined to control both the uniformity of the particle size and the copolymer composition on the basis of a theoretical calculation.[12] The density of functional groups present on the particle surfaces was quantified by time-dependent conductometric titration experiments. The time-dependent titration results revealed that carboxyl group surface coverage could vary from 0 to 100% as the MAA amount was varied during the semicontinuous polymerization process.[13] Table I lists the basic characterization results of the model P(BMA/BA) latex particles with a particle size about 250 nm in diameter.

Preparation of the pigmented latex films

In the case of the air-dried films to be prepared for the morphology study, films were cast from a pigment slurry/latex blend consisting of GCC pigment particles and cleaned P(BMA/BA) latex particles. The concentration of GCC was varied from 0 to 60 vol %, and the surface coverage of the carboxyl groups on P(BMA/BA) latex particles was varied from 0 to 100%.
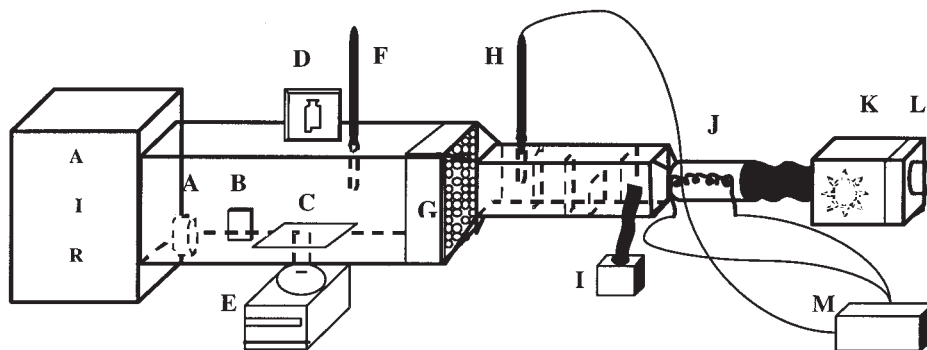
Figure 1 Schematic diagram of the wind tunnel used in the drying experiments: (A) vane anemometer, (B) hygrometer, (C) platform, (D) digital camera, (E) top loading balance, (F) thermometer, (G) straws for laminar flow, (H) temperature-sensing element, (I) humidifier, (J) heater, (K) fan, (L) air filter, and (M) thermostat.[18]

The pH was measured with a pH meter (model 125, Corning, Medfield, MA). The pH of the cleaned latex was adjusted to 9 by the addition of an aqueous ammonium hydroxide solution (NH_4OH) drop by drop into the latex with stirring. The pH of the pigment slurry/latex blend was measured to be 9 before film formation. After the removal of a certain amount of water with a Rotavapor apparatus (model EL 131, Büchi, Flawil, Switzerland) to attain a specific concentration of solids (~15%), films were cast by latex/pigment blends being dried on clean glass plates covered with Tedlar [poly(vinyl fluoride); DuPont, Wilmington, DE] films and the films being allowed to dry at room temperature.

In the studies of the drying kinetics, the pigmented latex blends were dried inside a wind tunnel in which the drying conditions could be well controlled (temperature within ±0.5°C, relative humidity within ±1%, and air velocity within ±1 cm/s). Figure 1 shows the schematic setup of the wind tunnel used in the drying experiments. The pigment/latex blends consisted of 35 wt % GCC particles and 65 wt % P(BMA/BA) latex particles. The concentration of solids for all the pigment/latex blends was adjusted to 4.0%. Here, the concentration of solids was kept low so that a distinctive constant-rate period and falling-rate period could be observed in the studies of the drying kinetics. For each set of samples to be compared, the same initial weight of the blend was used (2.5 or 2.8 g). The dispersions were spread on individual glass-slide surfaces covered with Tedlar film by the slight tilting of the glass slides so that the blends could spread over and cover the whole substrate surface with identical surface areas (19.36 cm^2). The platform on which the glass slide was placed was leveled on a top loading balance. Immediately after the spreading of the pigment/latex blend on the slide, the weight of the drying sample and drying time were recorded, and pictures of the drying sample were taken with a digital camera. The air velocity, relative

humidity, and temperature were measured with a Vane anemometer (Davis Instrument Manufacturing Co., Baltimore, MD), a hygrometer (Abbeon CAL, Inc., Santa Barbara, CA), and a mercury thermometer, respectively. The drying experiments were conducted at a relative humidity of approximately 27%.

Film characterization

An SEM examination of the films was conducted with a 6300f scanning electron microscope (JEOL USA, Inc., Peabody, MA) operated at an accelerating voltage of 1 kV. Pigment/latex blend films with thicknesses ranging from 0.25 to 0.28 mm were immersed in liquid nitrogen for 1 min and then fractured. Fractured films were glued to the SEM sample holder with double-sided carbon tape with the fracture surface facing upward. The sample holder was then inserted into the SEM chamber. SEM micrographs were taken of the cross-sectioned surface of the films, as depicted schematically in Figure 2. Images were recorded near the center of the fractured surface.

RESULTS AND DISCUSSION

Drying behavior and drying kinetics of the pigmented latex films

Pigmented latex films were dried in a wind tunnel in which the drying conditions could be well controlled and maintained.[18] Under well-controlled drying conditions (30°C and 25–27% relative humidity), the pigment/latex films dried in approximately 300 min. This drying period could be divided into two regions: the first 150–160 min of drying and the remaining 140–150 min. In the first region, each film dried uniformly until a dried spot appeared in the wet film. Then, in the second region, the area of the dried spot increased with time to the edge of the film. The edges of the wet film were the last area to be dried. Typical digital
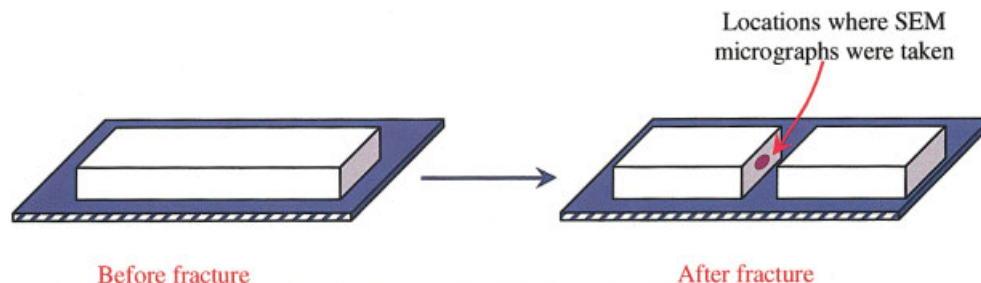
Figure 2 Illustration of the location at which SEM micrographs were taken of the freeze-fractured cross-sectional surface of a pigmented/latex film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

photographs of the drying pigmented blend files as a function of the drying time are shown in Figure 3.

During the drying process, a drying front that propagated from the center to the edge of the slide was observed. This observation was not unexpected because a concave meniscus was formed when the dispersion was placed in a well on the glass slide prepared with adhesive foam-backed mounting tape (Scotch, 3M, St. Paul, MN; see Fig. 3). This finding is similar to that of Winnik and Feng.[4] In their article, the authors pointed out that drying was complete in the thinnest region of the film in which there was less water present from the beginning of the drying process.

Influence of the number of carboxyl groups present on the latex particles on the drying kinetics of the pigment/latex blends

The method used here to evaluate the drying behavior and kinetics of the pigment/latex blends was to com-pare the total drying time needed to evaporate a specific amount of water (e.g., 99%). Films obtained from different pigment/latex blend samples, with identical parameters except for one variable (e.g., carboxyl group concentration on the latex particle surfaces), were investigated. Later, the drying rates were calculated from profiles of the weight loss versus time.

Table II shows the drying time for two pigment/latex blends, with the only difference being the carboxyl group surface coverage on the P(BMA/BA) latex particles. This table shows that the drying time needed to evaporate 99% of the water from the blend decreased as the number of carboxyl groups present on the latex particles increased, indicating that the neutralized carboxyl groups on the latex particles enhanced the drying rates. Figure 4 shows the drying kinetics of two series of pigmented blends dried inside the wind tunnel. Changes in the drying conditions did not change the overall trend: the presence of carboxyl
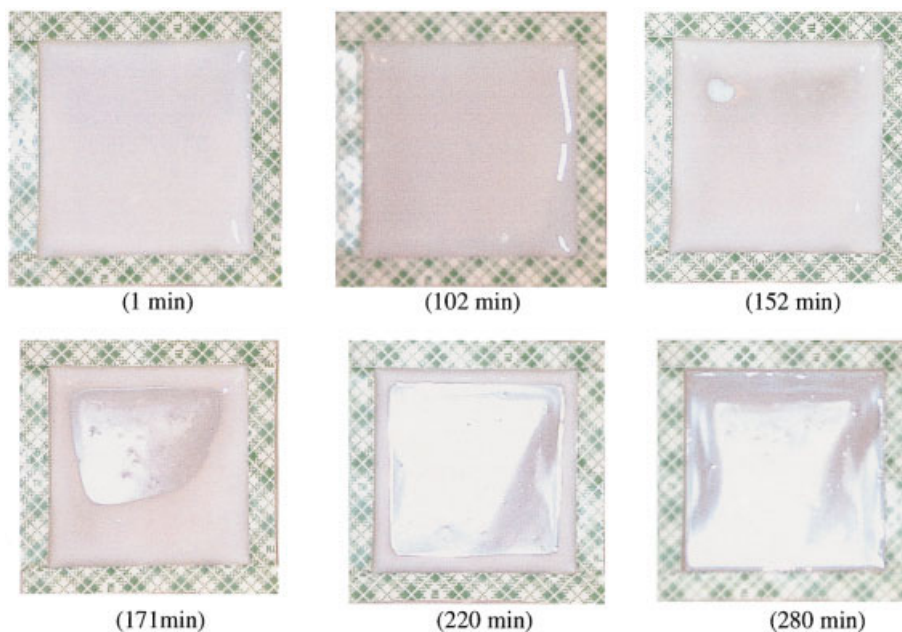
Figure 3 Drying profiles of pigmented latex films (pictures taken with a digital camera) under well-controlled drying conditions as a function of the drying time (sample 1: 35/65 w/w, initial weight = 2.5 g, initial percentage of solids = 4.0%, temperature = 30°C, relative humidity = 27%, air velocity = 63.8 cm/s). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Drying Time Needed to Evaporate 99% of the Water from GCC/P(BMA/BA) Blends

Blend sample	—COOH surface coverage on latex particles	Time to evaporate 99 wt % water (min)	D (cm²/s)
1	0	291	1.5×10^{-6}
2	100	250	1.9×10^{-6}

Drying conditions: GCC particle/latex particle sample = 35/65 by weight; initial weight = 2.5 g; initial solid = 4.0%; temperature = 30°C; relative humidity = 27%; air velocity = 63.8 cm/s; water diffusion (D) results from Guigner et al.[17]; D from domain II = 8.7×10^{-7} cm²/s; system: concentrated oil-in-water emulsion of poly(dimethylsiloxane) containing a crosslinker; drying conditions = 23°C; relative humidity = 50%.

groups on the latex particles could facilitate the drying process of the blend films.

Figure 5(a) presents a plot of the water loss as a function of the square root of time that may be used to further analyze the drying kinetics of the pigment/latex blends. In this figure, three domains can be distinguished in the curves. Domain I represents the beginning of the drying process and is nonlinear; domain II is linear in a water-loss region from 35 to 80% and ends after 180 min. The departure from linearity corresponds to the end of the first region in the macroscopic drying mechanism. The remaining water is lost in domain III, which is nonlinear once again and in which the drying rate strongly decreases, especially after 95% water loss.

According to Crank,[14] the linear part of the curve (domain II) can correspond to a mechanism of water loss by diffusion through a top layer of increasing thickness with a constant diffusion coefficient (D), as described in eq. (1):

$$\frac{M_1}{M_\infty} = \frac{2(Dt)^{1/2}}{L\pi^{1/2}} \qquad (1)$$

where M_t, M_∞, t, and L are the mass of water evaporated at time t, the mass of water evaporated at equilibrium, the time, and the initial thickness of the film (cm), respectively.

Figure 5(a) shows that blends composed of latex particles containing carboxyl groups exhibited much larger D values for water in domain II than the blend prepared with latex particles with no carboxyl groups present.

As illustrated in Figure 5(b), the calculation of the drying rate from a profile of the weight loss versus the drying time also supports the observation that carboxylated latex blends have a higher drying rate than noncarboxylated latex blends after an almost identical initial drying-rate period. During the constant-rate

drying period, water that is unbound to both latex and pigment particles evaporates as if the solids (latex or GCC particles) were not present. In the falling-rate drying period, however, water will have to diffuse through a dry, porous layer formed by the pigment particles and deformed latex particles, as shown in Figure 6, before it can evaporate into the atmosphere.[2,19,20] As calculated previously, D of water in carboxylated latex/pigment blends is higher than that in noncarboxylated latex/pigment blends. The reason for this is that regions with reduced chain mobility (RRCMs) will form as a result of the neutralization of —COOH before film formation occurs.[13] Higher carboxyl group surface coverage leads to a higher volume fraction of RRCMs, and this means that less soft latex polymer binder will be available for deformation. Soft

(a)

(b)
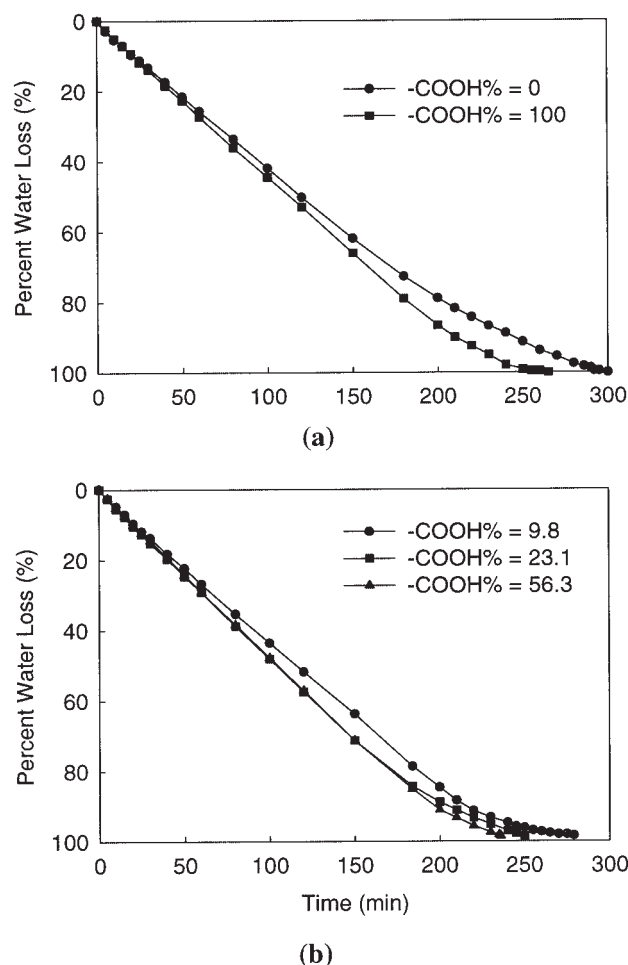
Figure 4 Comparison of the water loss versus time from drying experiments for samples prepared with different degrees of carboxylation in latex particles (sample: GCC particle/latex particle = 35/65 w/w, air velocity = 63.79 cm/s, initial percentage of solids = 4.0%, temperature = 30°C): (a) initial weight = 2.5 g and relative humidity = 27% and (b) initial weight = 2.8 g and relative humidity = 25%. —COOH% represents the carboxyl group surface coverage on the latex particles.

(a)

(b)
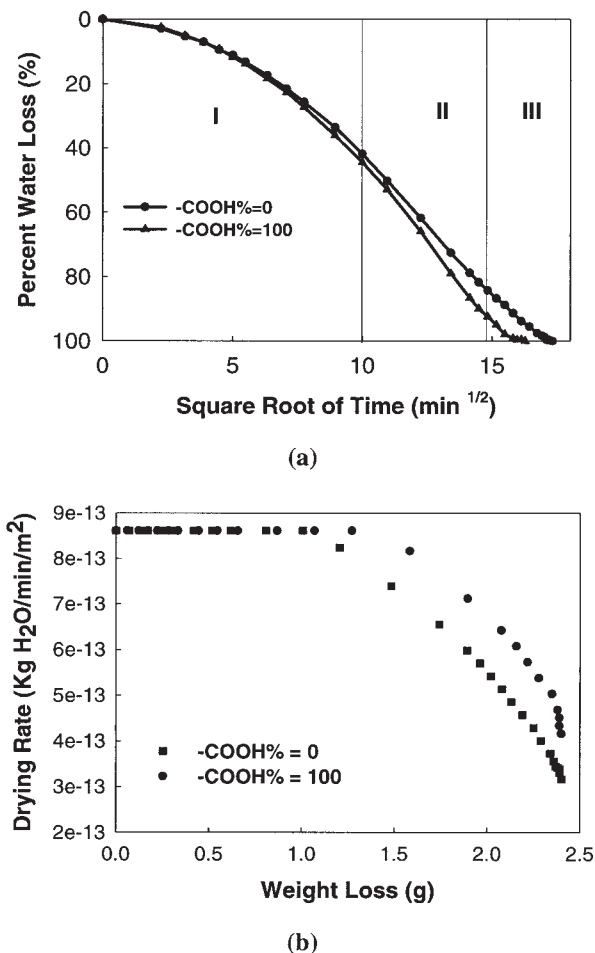
Figure 5 (a) Water loss versus the square root of time and (b) drying rate as a function of the weight loss of the pigment/latex blend systems (sample: GCC particle/latex particle = 35/65 w/w, initial weight = 2.5 g, initial percentage of solids = 4.0%, temperature = 30°C, relative humidity = 27%, air velocity = 63.8 cm/s). —COOH% in the legend represents the carboxyl group surface coverage on the latex particles.

polymers are able to more easily deform and close off small capillaries during the film-formation process, and this reduces water diffusion.[15] Therefore, for latex/pigment blends prepared with lower degrees of carboxylation, more soft binder polymer will be available, reducing the extent of water diffusion and thus yielding a smaller D value and an increased drying time.

Influence of the amount of stabilizer present in the system on the drying kinetics of the pigmented latex blend

In Table III and Figure 7, the effect of the amount of the stabilizer in the system on the drying kinetics is presented. When the stabilizer amount in the system decreased, the dispersion dried faster. This difference
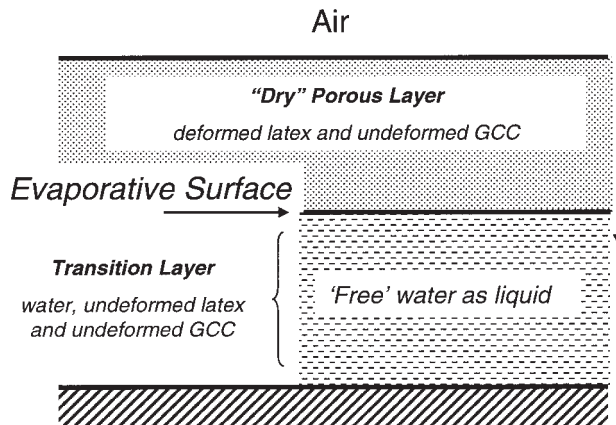
Figure 6 Illustration of the structure of a film formed as water evaporates from a GCC/latex blend during the falling-rate drying period, similar to Croll's view of the drying process.

in the drying rate resulted from the additional retention of water in the system when more hydrophilic NaPA stabilizer was present. Therefore, the drying rate was retarded when there was a larger amount of the stabilizer present in the system. The drying-rate profile is shown in Figure 7(b). There was a noticeable difference in the drying rates, especially between the 36% NaPA surface coverage sample and the other two. The sample with 36% NaPA coverage on the latex particles even exhibited a lower initial drying rate than the other two samples, and this indicated a strong retention effect of the stabilizer.

Influence of the PVC on the drying kinetics of the pigmented latex blends

The influence of the PVC on the drying kinetics is shown in Table IV and Figure 8. In general, when the PVC in the system was increased, the blend dried faster. However, in domain II, samples with lower PVC seemed to have a higher diffusion rate of water, as indicated by Figure 8(a). The D calculation results are shown in Table IV. There were two effects that reflected the presence of the filler. First, in domain II,
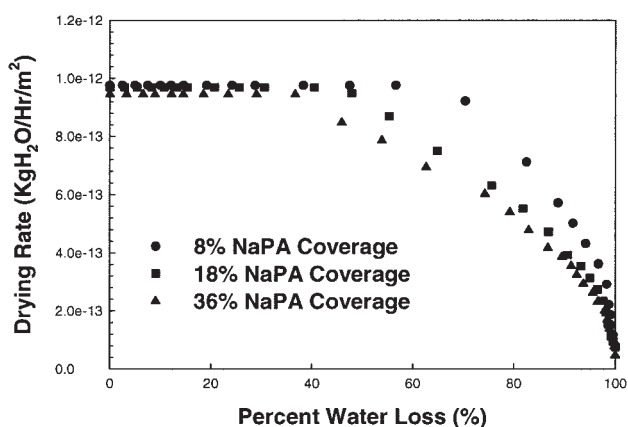
TABLE III
Drying Time Needed to Evaporate 99% of the Water from GCC/P (BMA/BA) Blends

Blend sample	Initial NaPA surface coverage on latex particles (%)	Time to lose 99 wt % water (min)
1	8	255
2	18	320
3	36	355

Drying conditions: GCC particle/latex particle sample = 35/65 by weight; temperature = 30°C; relative humidity = 27%; air velocity = 63.8 cm/s.
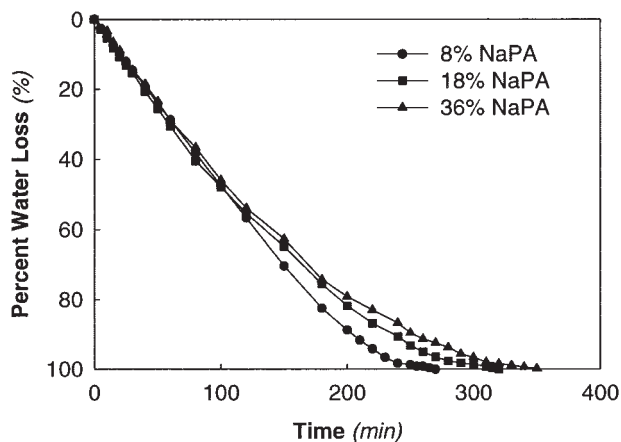
(a)

(b)

Figure 7 (a) Water loss versus time and (b) drying rate versus the water loss (%) obtained from drying experiments for three samples with different initial stabilizer coverage on latex particles (drying conditions for the sample: GCC particle/latex particle = 35/65 w/w, initial weight = 2.5 g, initial percentage of solids = 4.0%, temperature = 30°C, relative humidity = 27%, air velocity = 63.8 cm/s, carboxyl group coverage on latex particles = 56.3%).

the presence of hard particles increased the tortuosity of the path taken by water leaving the wet film, and this could account for a lower D value of water in the
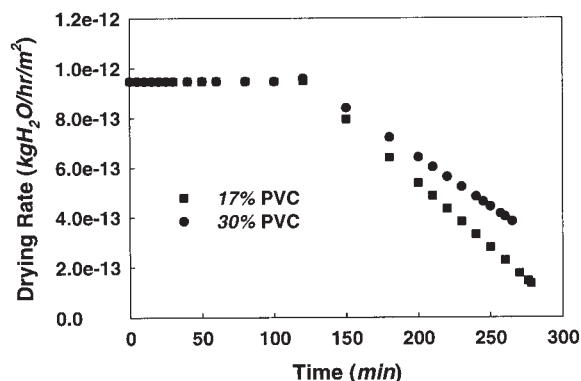
TABLE IV
Drying Time Needed to Evaporate 99% of the Water from GCC/P(BMA/BA) Blends

Blend sample	PVC (%)	Time to evaporate 99 wt % water (min)	D (cm^2/s)
1	17	260	1.83×10^{-6}
2	30	248	1.63×10^{-6}

Drying conditions: GCC particle/latex particle sample = 35/65 by weight; initial weight = 2.5 g; temperature = 30°C; relative humidity = 27%; air velocity = 63.8 cm/s; —COOH surface coverage on latex particles = 23.1%.
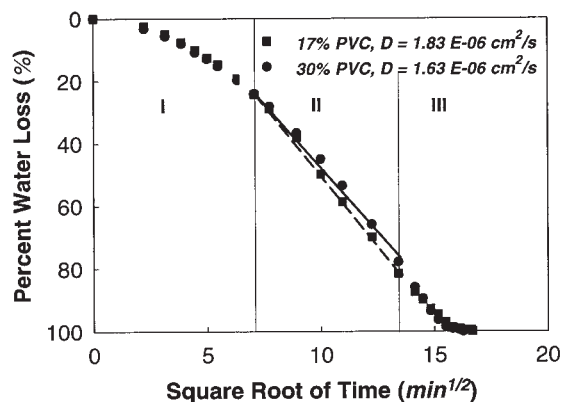

(a)

(b)

Figure 8 (a) Water loss versus time obtained from drying experiments and (b) water loss versus the square root of time (drying conditions for the sample: GCC particle/latex particle = 35/65 w/w, initial weight = 2.5 g, temperature = 30°C, relative humidity = 27%, air velocity = 63.8 cm/s, —COOH surface coverage on latex particles = 23.1%).

region when PVC increased. However, higher PVC values indicated a lower number of soft latex particles that could deform, so the magnitude of the transport of water would be increased. This would explain the increase in the drying rate during the falling-rate period when the PVC was higher. As shown in Figure 8, the net effect of PVC in the blend system was that a higher PVC led to shorter drying times.

Bulk morphology of the pigmented latex films

The bulk morphology of films prepared from the latex/pigment blends was studied with SEM and a freeze-fracture technique. The general characteristics of the SEM micrographs taken from the freeze-fractured cross section of the pigmented latex films were the existence of white regions distributed on a dark background. The white (light) spots or domains on the SEM micrographs represented the calcium carbonate particles or their aggregates, which were distributed
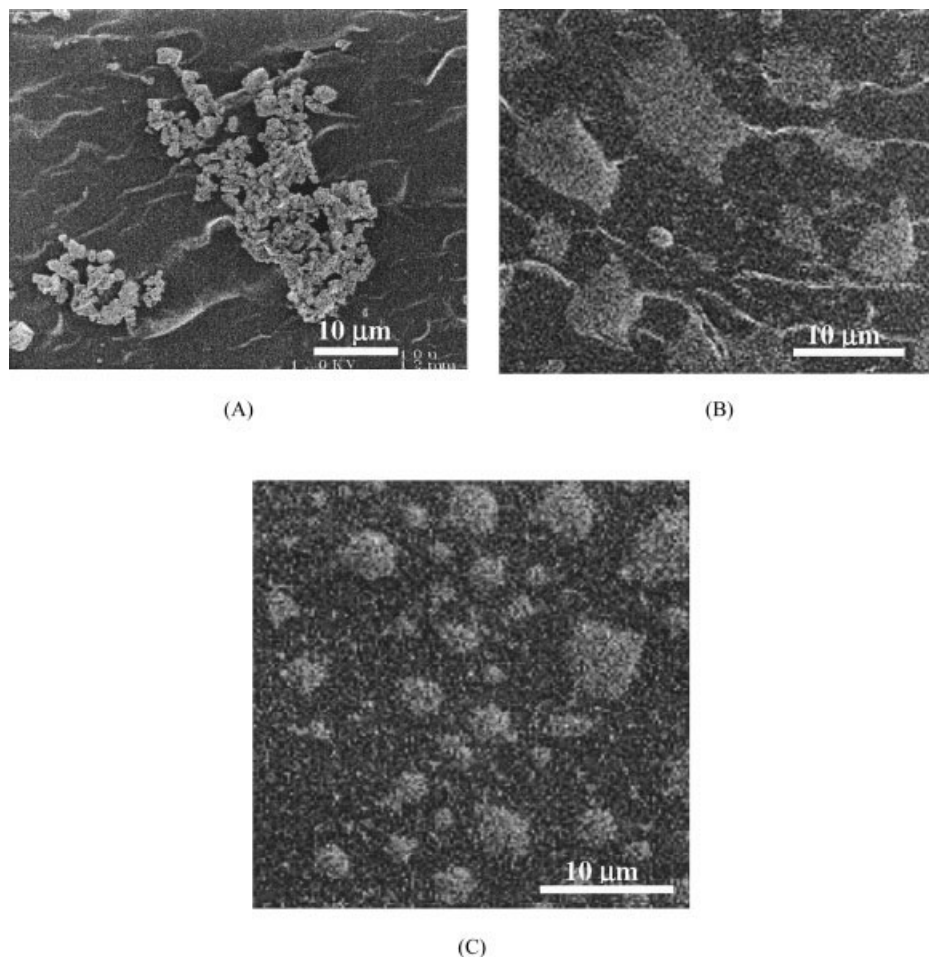
Figure 9 SEM micrographs of the freeze-fractured surfaces of pigmented latex films prepared from latex/pigment blends with different degrees of carboxylation on the latex particles. The surface coverage of the latex particles was (A) 0, (B) 23.1, and (C) 100% ([GCC] = 35 wt %, D_v for latex particles = 250 nm). D_v = volume-average particle diameter.

within the P(BMA/BA) copolymer matrix (the dark background).

Effect of the degree of carboxylation of latex particles on the bulk morphology of the pigmented latex films
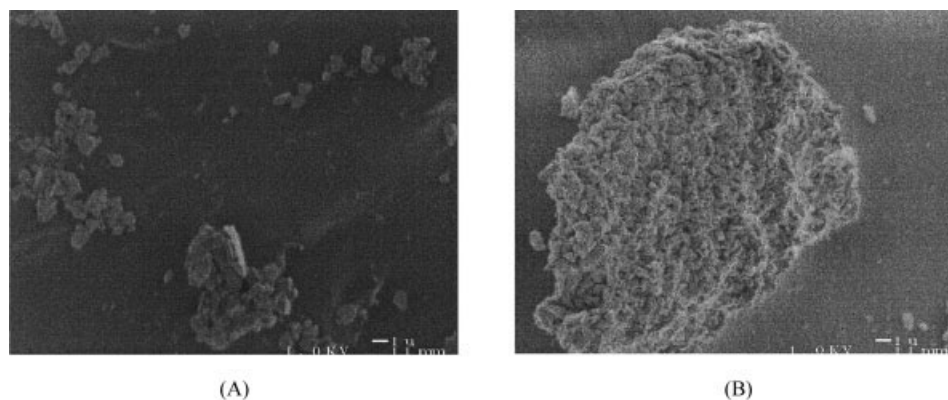
SEM micrographs taken of cross-sectioned film samples obtained from latex/pigment blends with different surface coverage of carboxyl groups on the surface of the latex particles are shown in Figure 9.

Smaller pigment particle aggregates were observed when the surface coverage of carboxyl groups was increased. The average domain size of the pigment particles decreased from around 10–15 μm to approximately 3–5 μm when the surface coverage of the carboxyl groups on the latex particles was increased from 0 to 100%. This indicated that the presence of the carboxyl groups improved the phase compatibility of the GCC and P(BMA/BA) polymers and prevented the formation of large pigment particle clusters or aggregates. Meanwhile, the pigment particle aggre-

gates exhibited a more uniform size distribution when the degree of carboxylation on the latex particles was higher.

Another interesting phenomenon that was observed was that when the latex particle samples had a relatively high carboxyl group surface coverage, the pigment particles or their aggregates became more difficult to observe in the SEM micrographs. However, the pigment particle aggregates were buried under the soft polymer matrix. This implied that fracture took place within the soft matrix instead of at the interface between the pigment particle aggregates and the soft polymer matrix. This indicated that the carboxyl groups present on the latex particles could strengthen the interface region and make it stronger than the soft polymer matrix, resulting in cohesive fracture occurring inside the polymer phase. The strengthening of the interphase by the presence of the carboxyl groups on the particles could be explained by the ionic interactions in the interphase.

Figure 10 SEM micrographs of the freeze-fractured surfaces of pigmented latex films prepared from latex/pigment blends with different latex particle sizes. The latex particle size was $D_v = 150$ nm in film A and $D_v = 450$ nm in film B. The surface coverage of the carboxyl groups on the latex particles was 0%. D_v = volume-average particle diameter.
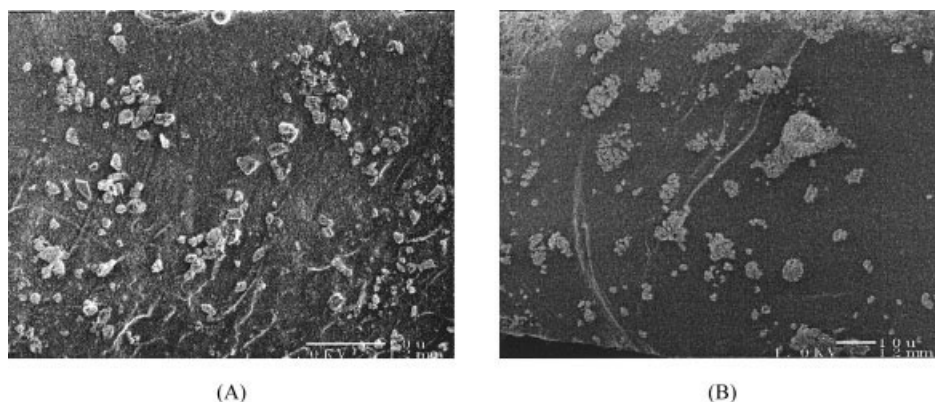
Effect of the latex particle size on the bulk morphology of the pigmented latex films

SEM micrographs taken from film samples prepared from latex/pigment blends with different latex particle sizes and no carboxyl groups present on the surface of the latex particles are shown in Figure 10.
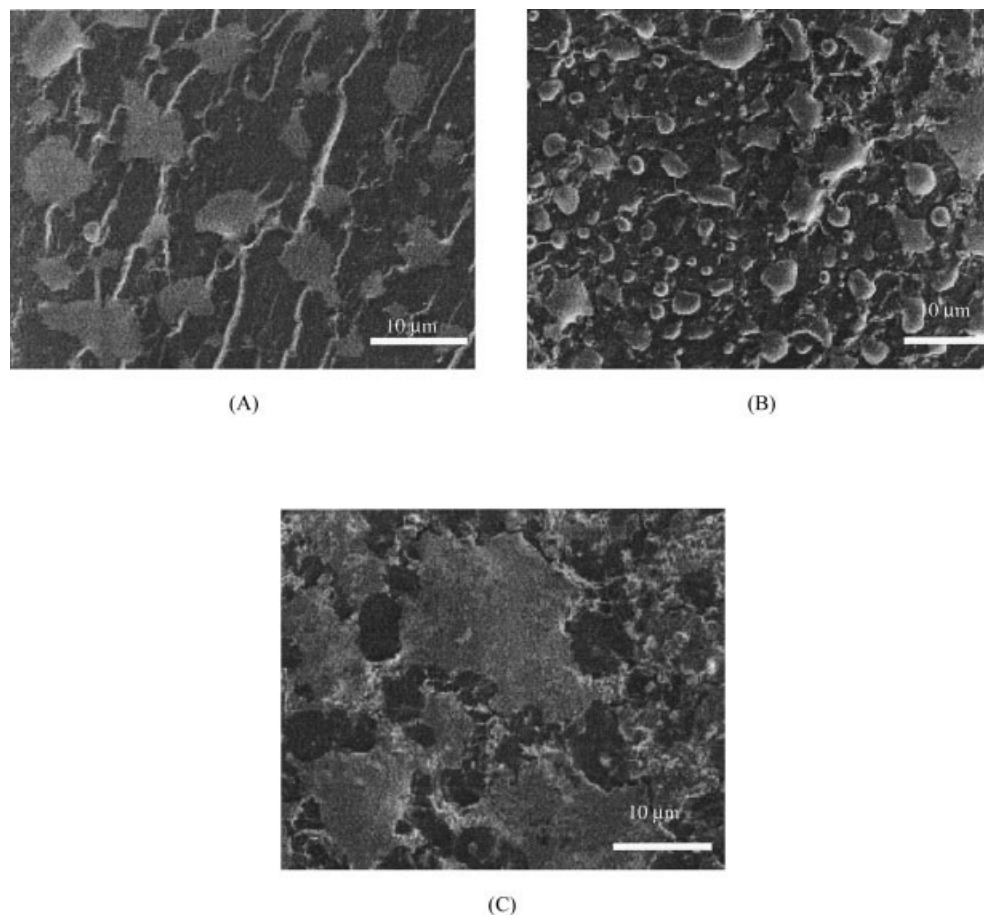
When latex particles in the latex/pigment were larger, the pigment particles formed larger aggregates that were distributed less evenly in the polymer matrix. As pointed out in another article,[13] smaller latex particles could help the system achieve better interactions between the GCC pigment particles and the latex particles because of the higher total surface area. Figure 11 shows similar trends when the latex particles possessing carboxyl surface groups increased in size in the latex/pigment blend. At the same time, these micrographs depicted in Figures 10 and 11 verified the effects of the degree of carboxylation of the latex particles.

Effect of the stabilizer amount on the bulk morphology of the blend films

SEM micrographs taken from cross-sectioned film samples from latex/pigment blends with different amounts of stabilizer present in the blend system are shown in Figure 12. When the initial stabilizer coverage on the latex particles was varied from 8 to 36%, the GCC particle aggregates were smallest when the initial NaPA coverage was 18%. The average domain size of the pigment particles decreased from around 6–7 μm to approximately 3–5 μm when the initial surface coverage of the stabilizer on the latex particles increased from 8 to 18% and then increased to more than 10 μm after the initial NaPA coverage became 36%. This observation agreed with the results obtained from the mechanical property measurements. When the surface coverage of NaPA on the latex particles was 18% initially, both the yield strength and tensile strength

Figure 11 SEM micrographs of the freeze-fractured surface of pigmented latex films prepared from latex/pigment blends with different latex particle sizes. The latex particle size was $D_v = 150$ nm in film A and $D_v = 450$ nm in film B. The amount of MAA used in the latex synthesis was 3 wt % with respect to the total comonomer. D_v = volume-average particle diameter.

Figure 12 SEM micrographs of the freeze-fractured surface of pigmented latex films prepared from latex/pigment blends with different amounts of the NaPA stabilizer present in the system. The surface coverage of NaPA on the latex particles was (A) 8, (B) 18, and (C) 36% ([—COOH] = 23.1%, [GCC] = 35 wt %, D_v for latex particles = 250 nm). D_v = volume-average particle diameter.

were higher than those obtained for samples prepared with 8 and 36% NaPA surface coverage.

When the initial NaPA coverage was as high as 36%, as the water evaporated from the system, the aqueous concentration of NaPA increased. When the aqueous concentration reached a critical concentration of NaPA for bridging flocculation of pigment particles to occur, the pigment particles were still able to move about freely because there was still enough water present in the system. This led to the formation of larger aggregates. However, in the case of lower initial NaPA coverage, when the aqueous concentration of NaPA reached the critical concentration of NaPA for bridging flocculation of the GCC, the pigment had less mobility in the system because at that time, the water remaining in the system was much lower than that of the 36% case. This was the reason that there were no large GCC particle aggregates formed in the cases in which 8 and 18% initial NaPA coverage was employed. Smaller GCC aggregates that occurred in the case of 18% NaPA coverage in comparison with the 8% coverage case could be explained by the better

dispersing ability of NaPA when there was more stabilizer present in the system.

CONCLUSIONS

In this study, the drying kinetics and bulk morphology of pigmented latex films were examined. A two-stage drying process was observed for blend films dried in a wind tunnel: a uniform drying stage of the wet film followed by an expansion stage of the dry portion. Overall, pigment/latex blends with higher degrees of carboxylation dried faster. A detailed analysis of the drying kinetics revealed that water diffused much faster if the latexes were carboxylated. RRCMs in the pigmented latex films reduced the amount of soft polymer present, which could deform and close off small capillaries, with the net result being that the magnitude of the capillary transport of water was increased. This in turn increased the rate of diffusion of water through the films and allowed the films to dry faster. When the amount of stabilizer in the blend system was higher, the dispersion dried more slowly because of a water retention effect

resulting from the hydrophilic nature of the stabilizer. PVC had two effects on the drying kinetics of the pigment/latex blend films: increasing the tortuosity of the path taken by water leaving the wet film and reducing the number of soft latex particles that could deform. The net effect of PVC in the blend system was that the drying time was shortened when the PVC increased.

SEM imaging showed that an increased degree of carboxylation for the latex particles in the latex/pigment blends resulted in the formation of smaller pigment aggregates and a more even size distribution of the pigment aggregates in the blend films. Smaller latex particles reduced the pigment aggregate size because of the larger surface area of the latex particles. When the initial stabilizer coverage on the latex particles was equal to 18%, smaller aggregates of GCC were distributed in the polymer matrix of the blend films in comparison with the cases in which the initial stabilizer coverage on the latex particles was 8 or 36%.

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