# Study of the Drying Behavior of Model Latex Blends during Film Formation: Influence of Carboxyl Groups

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SUMMARY: Latex blending is a strategy used to eliminate volatile organic compounds from latex coatings formulations. This paper focuses on the study of the drying kinetics of model hard/soft latex blends and the influence of the presence of carboxyl groups on these particles as well as the extent of neutralization of the carboxyl groups with different bases. The model latex blend was comprised of clean, well-defined polystyrene hard and poly(*n*-butyl methacrylate-co-*n*-butyl acrylate) soft latex particles with monodisperse particle sizes, homogeneous copolymer composition, and independent control of particle size and carboxyl group content. Drying models are discussed. It was found that the presence of carboxyl groups in the latex particles retarded the drying rate of the model latex blends. When the carboxyl groups present in the latex blends with low carboxyl group coverage on polystyrene particles were neutralized by using ammonium hydroxide or sodium hydroxide, the drying rate increased. When the carboxyl groups present in the latex blends with a high carboxyl group coverage on polystyrene particles were neutralized by sodium hydroxide, potassium hydroxide, or cesium hydroxide, the drying rate first decreased and then increased as the extent of the neutralization increased. However, the neutralization of these carboxyl groups with ammonium hydroxide increased the drying rate of the latex blends within a broad range of neutralization conditions (from 0 to 100%). A cluster model was proposed to explain these phenomena.

## Introduction

Perhaps the most important advantage of latex coatings compared to their solvent-based counterparts is the decreased environmental impact of the water-borne coatings. Limits have been placed on the emission of volatile organic compounds (VOCs). A large portion of the VOCs that are currently released into the atmosphere are emitted from paints and coatings. It is now believed that the emissions of VOCs are the major cause of photochemical smog and ozone pollution. In response to these environmental protection requirements, the coatings industry is gradually replacing solvent-based coatings with water-based systems[1,2].

However, most current latex coatings only decrease the VOC emissions instead of completely eliminating them because volatile organics are still commonly used to promote the coalescence of latex particles during the film formation process[1]. Polymers with low glass transition temperatures ($T_g$) are easily deformed and the polymer chains are able to interpenetrate through the boundaries between adjacent latex particles during the drying of the latex. This type of latex has excellent film formation ability. Unfortunately, because of the low $T_g$, the film produced will be tacky to the touch and have low mechanical strength. If the latex is comprised of high $T_g$ polymer, then the compliance is too small for the forces which operate during the drying process (e.g., capillary pressures) to deform the particles into a continuous film. The traditional solution to this problem has been to add volatile organic plasticizers to the dispersion of polymer particles with high glass transition temperature to temporarily decrease the $T_g$ of the polymers and promote deformability[1,3]. To recover the good block resistance and mechanical performance possessed by the high $T_g$ polymers, these coalescing aids have to evaporate from the latex polymer film after the film has formed, which results in VOC emissions. Thus, new strategies to form latex films with good mechanical properties and block resistance without the addition of coalescing solvents are in demand.

The use of latex blends is the most attractive strategy to solve this problem[4-7]. In such latex blends (i.e., hard/soft latex blend system), it is envisioned that the soft latex particles (low $T_g$) will deform and form a film to create a continuous phase to which the hard latex particles (high $T_g$) will impart desirable mechanical or optical properties. Polymer latex blends are thus expected to offer a compromise between latexes that are good film formers and whose films possess good mechanical properties[8]. Such latex blends would not require volatile solvent plasticizers, and therefore, would be less damaging to the environment. Moreover, it is known that mixtures of spherical particles of controlled size can "self-assemble" into superlattices as a result of entropic contributions[9]. This phenomenon opens up the possibility of creating latex films with controlled microstructures. Therefore, a deeper understanding of the fundamental parameters governing latex film formation, particle morphologies, and their relationship to the properties of films prepared in the absence of the undesirable formulation additives is necessary.

The properties and morphologies of films cast from latex blends are influenced by parameters which can be classified as being either geometrical (e.g., particle size and particle size ratio between the component latex particles), physical (e.g., glass transition temperature, volume fraction, and compatibility), chemical (e.g., surface charge and surface functional groups), or environmental (e.g., drying temperature, humidity, and air velocity during drying). While the strategy of using latex blends is being actively investigated in industry, theoretical studies are just beginning. Several papers have reported on investigations concerned with the influence of some of the geometrical or physical parameters[4,5,10] such as particle size and $T_g$ on film formation or on film properties. However, few papers have reported on studies of the chemical or environmental parameters that influence film formation. Even fewer publications are related to the drying behavior of latex blends. This paper focuses on the investigation of the influence of the carboxyl groups present on the latex particles, and the neutralization of these carboxyl groups by different bases, i.e., chemical parameters, on the drying behavior of model latex blends during the film formation process.

## Experimental

### Materials

*n*-Butyl methacrylate (BMA), *n*-butyl acrylate (BA), styrene (St), and methacrylic acid (MAA) monomers (Aldrich; reagent grade) were purified by passing them through columns filled with an appropriate inhibitor removal packing material (Aldrich). Maleic acid (MA; Aldrich; analytical grade), sodium dodecyl sulfate (SDS; Fisher Scientific; reagent grade), Aerosol MA-80 (Cytec Industries), potassium persulfate (KPS; Aldrich; reagent grade), sodium bicarbonate (Aldrich; reagent grade), sodium hydroxide (Fisher; reagent grade), ammonium hydroxide (28%; EM Science; reagent grade), and cesium hydroxide (CsOH; Aldrich; reagent grade) were used as received without further purification. Cationic ion exchange resin (AG 50W-X4, 20~50 mesh; Bio-Rad Company) was extensively washed with deionized (DI) water before use. Anionic ion exchange resin (AG 1-X4, 20~50 mesh; Bio-Rad Company) was converted from its chloride form to a hydroxide form using a 3 N sodium hydroxide solution, followed by complete washing of the resin with DI water to remove the sodium hydroxide just before use. The serum replacement process was also used to pre-clean some of the latexes[11].

## Synthesis and Characterization of Model Latex Particles

The detailed methods used for the synthesis, cleaning, and characterization of the model polystyrene (PS; non-carboxylated and carboxylated) and poly($n$-butyl methacrylate-co-$n$-butyl acrylate) [P(BMA/BA); non-carboxylated and carboxylated] latex particles are reported elsewhere[12]. P(BMA/BA) copolymer model latexes (non-carboxylated and carboxylated) were prepared by conventional semi-continuous emulsion polymerization processes at 80 $^{o}$C. All syntheses were performed in a 500 ml four-neck flask equipped with a reflux condenser, nitrogen gas inlet tube, PTFE stirrer (230 rpm), and two feed tubes for monomer and surfactant solution, respectively. The initial 1.5 hour period of the polymerization represents the seeding step where 10% of the monomer mixture (weight ratio of BMA/BA = 75/25) was used to prepare a in-situ seed latex. After the seed latex was almost fully formed (~ 95% conversion), the remaining monomer mixture (BMA, BA, and MAA for carboxylated latex particles) and surfactant solution were fed separately into the reactor at constant rates (i.e., 0.26 ml/min for the monomer mixture and 0.23 ml/min for the surfactant solution) using two syringe pumps (Harvard Apparatus 22). The monomer and surfactant feed rates were carefully calculated to obtain monodisperse latex particles with homogeneous copolymer composition[12]. When the feed process was completed, the reaction was allowed to continue for another two hours and the latex was allowed to cool to room temperature and was then filtered. Each of these carboxylated P(BMA/BA) latex particles obtained in the manner described above contains a small BMA/BA copolymer core with a volume fraction of around 0.1 and a thick BMA/BA/MAA copolymer shell (Fig. 1A). The copolymers in the core and in the shell have approximately the same glass transition temperature which was achieved by adjusting the copolymer compositions in the core and shell.

PS latex particles were prepared by shot growth batch[13,14] and conventional semi-continuous processes. The synthesis of carboxylated PS latex by a semi-continuous process was performed similarly to the methods described above. In the shot growth process, the polymerizations were carried out in 200 cm$^3$ pressure bottles. There were two stages for feeding the reactants in this process. In the initial stage, specific amounts of styrene, surfactant (Aerosol MA-80), sodium bicarbonate, and water were charged into the bottles. The contents of each bottle were purged with nitrogen using a hypodermic needle inserted through a rubber gasket in the bottle cap. The required amount of aqueous initiator solution (KPS) was purged with nitrogen and injected into each bottle using a hypodermic syringe.

The bottles were placed in cloth jackets and placed in a bottle polymerizer unit and rotated end-over-end in a thermostated bath heated at 70 °C for 1.5 hours. At this time, the conversion of styrene reached 95% according to a conversion vs. time curve which was determined independently. At this point, specific amounts of Aerosol MA-80, sodium bicarbonate, KPS, styrene, maleic acid, and water were injected into each bottle. The polymerization were continued for 13.5 hours. Each of these PS particle obtained above contains a large PS homopolymer core with a volume fraction of about 0.93 and a thin layer of St/MAA copolymer shell (Fig. 1B).

The PS and P(BMA/BA) latex particles which were obtained in the processes described above were then cleaned using the ion exchange method[16]. The cleaned latex particles were characterized by conductomitric titration (to determine the carboxyl group concentration on the latex particle surfaces or inside the particles), capillary hydrodynamic fractionation (Model 1100, Matec Applied Sciences; for particle size and size distribution), and transmission electron microscopy (Philips EM400T; for particle morphology)[12]. The characterization results for some of the PS and P(BMA/BA) model latexes which have been used in this work are listed in Table 1.
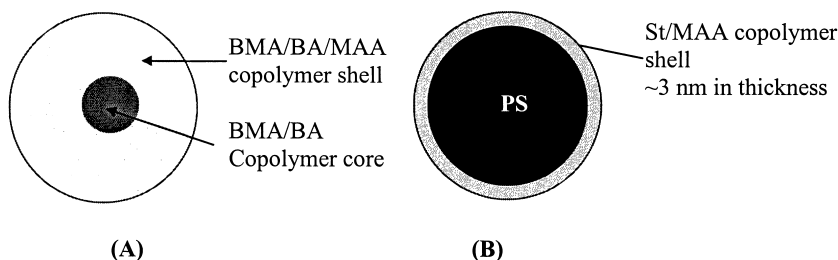


Fig. 1: The structures of the carboxylated model latex particles: (A) a carboxylated P(BMA/BA) soft latex particle; and (B) a carboxylated PS hard latex particle.

## Drying of Model Latex Blends

Most latex samples were dried inside a wind tunnel (built in this lab, Fig. 2) with good control of drying conditions [temperature: ± 0.5 °C, relative humidity (R.H.): ± 1%, and air velocity (A.V.): ± 1 cm/s]. Microglass slides (1" x 3") were used as the substrates for the drying experiments. A camera with close-up lenses was used to take pictures from the top of the

drying sample and graph paper was attached to the bottom of the slide to facilitate the measurement of the wet and drying edge areas. All latex blends were adjusted to an initial solids content of 4.0 wt.%. The latex blend was comprised of 35 wt.% PS (hard particles) latex and 65 wt.% P(BMA/BA) (soft particles) latex. For each set of samples to be compared, the initial quantities of dispersion (primarily 1.50 g) were weighed as identically as possible (± 0.25%). The dispersions were spread on the individual glass slide to produce wet films covering the whole substrate surface with identical surface areas (e.g., 19 $cm^2$) by slightly tilting the substrate. The platform on which the glass slide was placed was carefully leveled on a top loading balance. During the drying process, the weight of the drying sample, drying time, wet area, and drying edge area were recorded. Most measurements were repeated three times under identical drying conditions and averaged results are reported.

Table 1: Model latex particles that were used for the investigation of the drying behavior of latex blends during film formation

| Sample Code | PS hard latex particles | | | | | P(BMA/BA) soft latex particles | | | |
|---|---|---|---|---|---|---|---|---|---|
|  | S16 | SOOH 11 | SOOH 13 | SOOH 14 | Sc9 | BB2 | BBc2 | BBc1 | BBc3 |
| $D_n^a$ (nm) | 130.4 | 135.1 | 130.5 | 131.4 | 128.5 | 128.9 | 129.1 | 117.3 | 116.8 |
| $D_w^b$ (nm) | 132.9 | 139.2 | 134.7 | 134.6 | 131.0 | 131.4 | 130.8 | 120.4 | 118.1 |
| $PDI^c$ | 1.019 | 1.030 | 1.032 | 1.024 | 1.019 | 1.019 | 1.013 | 1.026 | 1.011 |
| $PCS^d$ | 0.00 | 84.3 | 61.1 | 66.6 | 88.9 | 0.00 | 56.9 | 40.0 | 23.6 |
| $CDS^e$ | 0.00 | 0.616 | 0.818 | 1.11 | 8.58 | 0.00 | 0.845 | 1.64 | 2.43 |
| $SAC^f$ | 0.00 | 5.54 | 7.36 | 10.0 | 77.2 | 0.00 | 7.60 | 14.7 | 21.9 |

[a] Number-average particle diameter
[b] Weight-average particle diameter
[c] Polydispersity index ($D_w/D_n$)
[d] Percentage of carboxyl groups localized on the particle surface compared to the total amount of carboxyl groups incorporated
[e] Carboxyl group density on particle surface ($COOH/nm^2$)
[f] Percentage of particle surface area covered by the carboxyl groups, using the value of 9 $Å^2$ as the cross-sectional area of each COOH group[15]

# Results and Discussion

To investigate the influence of the concentration of carboxyl groups present in the latex particles on the drying behavior of latex blends, influence of all other parameters has to be eliminated. Thus, all additives (e.g., surfactant, buffer, and initiator), by-products (e.g., water-soluble oligomers), and unreacted reagents (e.g., maleic acid) have to be removed by cleaning the model latexes. The latex particle sizes were also monodisperse and the latex polymers have homogeneous compositions to eliminate any size or composition effects. In other words, the only variable in this latex blend study is the carboxyl group concentration. Therefore, highly diluted latexes have to be used because of the poor stability of the completely cleaned latexes at high concentrations. Since most coating formulations contain latex dispersions at high solids levels (i.e., > 50 wt.%), most previous studies of the drying process began with dispersions at high concentrations. However, this present study is useful to investigate the influence of a specific parameter like the carboxyl group presence on drying kinetics and to carefully examine the early stages of drying, although little previous work has been carried out on the drying of highly diluted dispersions[17]. Here, the latex blends with 4.0 wt.% solids were quite stable before drying all of the samples that contained different concentrations of carboxyl groups on the latex particles. The average flux and time needed to lose specific amounts of water from samples of soft/hard latex blends were compared. When examining a given variable, samples prepared with identical initial wetted areas, initial solids contents, masses, and wet film thicknesses were compared, and the water loss rates, wet areas, and drying edge areas were measured under the same drying conditions, as controlled by the wind tunnel (Fig. 2).



A—Vane annemometer; B—Hygrometer; C—Platform; D—Camera; E—Top loading
balance; F—Thermometer; G—Straws for laminar flow; H—Temp. sensing element
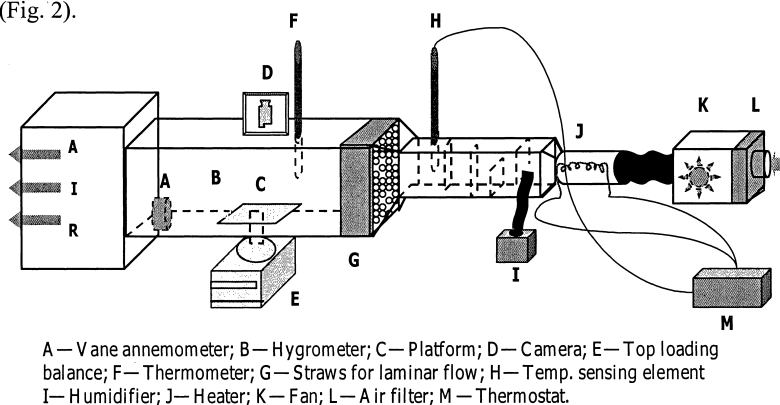I—Humidifier; J—Heater; K—Fan; L—Air filter; M—Thermostat.

Fig. 2: Schematic diagram of the wind tunnel which was used for the drying experiments.

## Drying Behavior of Diluted Dispersions and Drying Rate Calculations

Latex blends were prepared by mixing dispersions of a given type of hard latex particles (PS) with soft latex particles [P(BMA/BA)], each having similar particle sizes, but different amounts of carboxyl groups. When the latex blends were spread onto a flat glass surface, a flat liquid drop with a slightly convex surface formed spontaneously and covered the entire glass substrate surface. Drying occurs initially at the outermost region of the droplet and the drying region moves towards the center of the drop, forming a drying edge surrounding the wet film area (Fig. 3A). An example of data obtained from a typical drying experiment is shown in Fig. 3B. The first feature that one notices is that the cumulative water loss over 60% of the drying time (510 minutes) is linear. Accordingly, obvious shrinking of the wet film area starts at around the same time. The cumulative weight loss versus drying time data were statistically curve-fitted with a fifth-order polynomial function so that an instantaneous water evaporation rate could be readily computed for any value of elapsed time. $R^2$ values should be very near to unity with $|R^2\text{-}1| < 0.0001$. If $R^2$ falls outside this criterion, a sixth-order polynomial function should be fitted. The differentials of the functions fitted above yielded the instantaneous drying rate. To obtain the instantaneous evaporative flux or the drying rate per unit area of the wet latex film surface, the above drying rates were divided by the corresponding wetted areas, i.e., the non-transparent, non-coalesced, cloudy region of the drying latex blend. The wetted area used in the calculation includes the area of the obviously wet and milky latex film, and the small and narrow transition area (i.e., edge area) around the milky region. The instantaneous fluxes were then plotted as a function of drying time (Fig. 4). From Fig. 4, it can be seen that the flux curve is flat over a long portion (ca. 80%) of the drying time (510 minutes) and then increases rapidly. The transition point where the flux increases rapidly occurs later than the point when deviation from linearity on the cumulative weight loss vs. time curve shown in Fig. 3B is observed. It is assumed that the flat region of the flux curve represents the steady-state drying process. Therefore, the average fluxes can be calculated by the following equation:

$$Ave.\ Flux = C_w / (A \cdot t) \qquad\qquad (1)$$

where $C_w$ is the cumulative weight loss in grams, $t$ is the drying time in minutes, and $A$ is the average wet film area in $cm^2$. This average area here includes the wet latex film area before

the point when the instantaneous drying flux vs. time curve begins to deviate from the flat region.
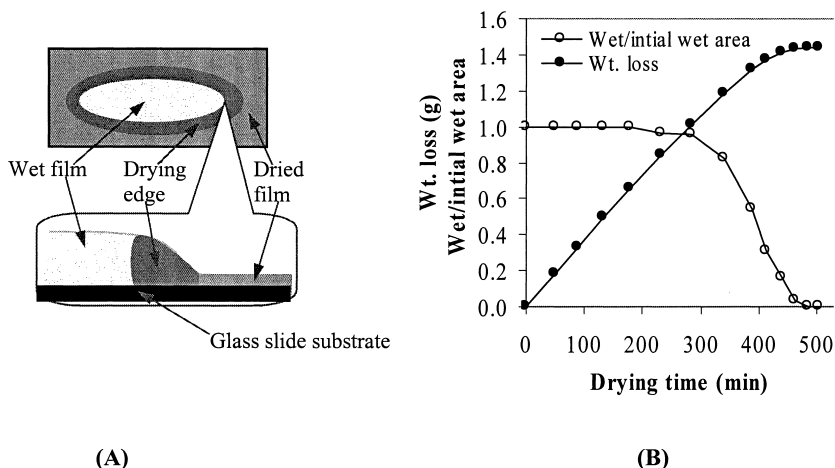


(A)   (B)

Fig. 3: (A) drying model; (B) Weight loss and the ratio of the wet area at any given time to the initial wet area as a function of drying time for a latex blend consisting of cleaned latexes (particle diameter ~120 nm): 65 wt.% of BMA/BA copolymer soft particles, 35 wt.% PS hard particles, 21.8% and 10.0% carboxyl group coverage on the P(BMA/BA) soft and PS hard particles, respectively. Initial wt. = 1.50 g, initial % solids = 4.0%; initial wet area =1 9 cm$^2$; Temp. = 23 $^{\circ}$C, R.H. = 55%, A.V. = 15.2 cm/s.

## Discussion of Drying Models

Latex drying models which are published in the literature assume that water evaporation occurs uniformly over the entire film surface. In all of our experiments, the latex blend films dried as a moving edge which surrounded the wet film area. The wet latex film shrunk and the edge moved towards the center of the wet film with a very small difference in propagating speeds in different directions when the substrate was aligned along the streamline of air in the wind tunnel. The edge stopped moving when the wet latex film area was very small; after this time, this small wet film disappeared. The area of the smallest wet film was recorded for each sample (Table 2). The propagating speed of the drying edge along the direction of the air streamline was a little bit faster than that observed opposite to the direction of the streamline. This phenomenon is different from that observed by Pramojaney[18] who noticed that the propagation of the drying front only took place along the direction of the streamline. The

main reason for this difference might be due to the low solids contents used for our experiments. Another possible reason might be the low air velocity (< 65 cm/s) which was used in this work. Although the moving drying edge occurring in the drying process of some latex dispersions has been mentioned previously,[18-22] the models of the drying process have not taken the drying edge into consideration.
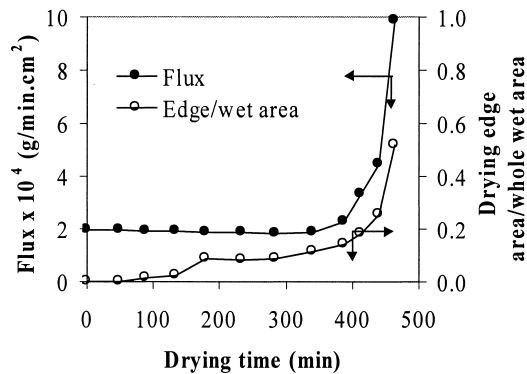


Fig. 4: Instantaneous flux and the ratio of the drying edge area to the wet area as a function of drying time for a latex blend. The characteristic of the latex blend and drying conditions are the same as described in Fig. 3.

The models that assume uniform drying over the entire wet film surface face problems in explaining the later stage instantaneous flux curves. As predicted by conventional drying theories, the instantaneous flux is supposed to drop during the falling-rate (later) stage, which is opposite to the experimental results (see Fig. 4). Some authors mentioned the possibility that the regions of the films which are assumed to be completely dried may still contain a considerable amount of moisture which evaporates slowly, and therefore, make the calculated flux higher than it is supposed to be[21-23]. However, based on our observations, we think that this is not the main reason for the increase in the flux in the later stages of the drying process. The water evaporation rate was measured immediately after the disappearance of the wet film area. This value should represent the maximum water evaporation rate from the dried region because the dried region area is at its maximum (i.e., the whole substrate surface) by that time. To estimate the contribution of the water evaporated from the dried region to the maximum increase in the flux, the drying rate of the dried region obtained above was divided by the smallest wet film area corresponding to each sample. Some of these values are listed in

Table 2. It is seen from Table 2 that the largest increase in flux which was contributed by the dried region is 2.08 x $10^{-4}$ g/min·cm$^2$, which is very small compared to the large increase in flux in the later stages of drying (usually 3 to 5 times or more larger than that of the constant portion). Therefore, the models which assume uniform drying can not be applied to the current latex blend experiments.

Table 2: Increase in flux from the evaporation of water from the dried regions of the latex films

| Latex blend | COOH coverage on hard particles (%) | COOH coverage on soft paritles (%) | Drying rate of "dried region" x $10^5$ (g/min) | Smallest wet area recorded (cm$^2$) | ΔFlux[a] x $10^4$ (g/min.cm$^2$) |
|---|---|---|---|---|---|
| SB10-2 | 0.0 | 0.0 | 3.74 | 0.20 | 1.85 |
| ScBc13a[b] | 10.0 | 21.9 | 1.23 | 0.96 | 0.13 |
| ScBc13b[b] | 10.0 | 21.9 | 1.52 | 0.90 | 0.17 |
| ScB2-3 | 7.36 | 0.0 | 1.76 | 0.50 | 0.35 |
| ScBc14a[c] | 10.0 | 21.9 | 0.52 | 2.24 | 0.02 |
| SBc1-1 | 0.0 | 7.60 | 0.83 | 0.04 | 2.08 |
| SBc3-1 | 0.0 | 21.9 | 4.29 | 0.35 | 1.22 |
| ScB1-3 | 5.54 | 0.0 | 1.15 | 1.61 | 0.07 |

[a] Increase in flux from the evaporation of water from the dried region of the latex films.
[b] the carboxyl groups were neutralized by ammonia in the ratio of [NH$_4$OH]/[COOH] = 1.15.
[c] the carboxyl groups were neutralized by ammonia in the ratio of [NaOH]/[COOH] = 1.19.
Drying temp. = 23 °C, Relative humidity = 55%, Air velocity = 15.2 cm/s. All latexes are cleaned, with particle diameters of 120 nm; all blends contain 35 wt.% PS and 65 wt.% P(BMA/BA); solids % of latex blend = 4.0%.

We propose that drying is not uniform even in the wet surface region. Drying may take place with different rates in the wet film. The wet film was then divided into two rate zones: (1) a uniform rate zone where the film appears to be homogeneously wet, and (2) an edge rate zone located between the apparent wet film and the dried film. The flux in the edge zone may be much faster than that found in the uniform wet surface zone, and the fast increase in the apparent instantaneous flux in the later stages of drying may be due to the very fast evaporation of water from the edge zone. To evaluate the flux from the edge zone, the ratio of the edge area to the entire wet area against the drying time was plotted and it was found that this curve matches the flux curve very well, especially in the later stages of drying (Fig. 4),

indicating that the flux in the edge zone is much faster than that observed in the uniform wet surface zone. This proposed mechanism can explain the fast increase in flux in the later stage of drying, which is mainly due to the rapid increase in the ratio of the edge area to the entire wet film area and the much faster water evaporation in the edge zone. This can also explain the observation that the deviation from the flat portion on the instantaneous drying flux vs. time curve started later than the deviation from the linear portion on the cumulative weight loss vs. time curve. One may have noticed from Fig. 4 that there is a small "jump" in the edge ratio curve from 0 to 0.09 at ~ 200 min of drying with no obvious change in the corresponding flux. This is the point that the drying edge can be observed from the top. Because of experimental limitations, the drying edge could not be measured and was treated as zero before that point. The drying edge can only be practically observed and recorded from the top of the film when it has propagated on the surface of the substrate. The drying flux over the edge zone might be calculated if the exact edge area could be measured. Investigations are currently being performed to clarify this point and results will be reported in a subsequent paper.

Because of the complexity of the drying behavior of model latex blends, which can not be adequately described only by using a drying rate, additional elements are required to express the drying behavior of a latex blend dried on a glass slide substrate. Thus, two methods were utilized to compare the drying kinetics of different latex blends. One is to compare the total drying time needed to lose a specific amount of water (e.g., 99%) from a film for different latex blend samples with identical parameters except for the one (e.g., carboxyl group content) to be investigated. This approach takes into consideration all of the different drying zones. The other method is to compare the average fluxes over the constant rate period (flat portion of Fig. 4) assuming that the evaporation from the edge zone is negligible because the ratio of edge area to wet area is very small during this period.

## Influence of Carboxyl Groups on the Drying Kinetics

Fig. 5 shows the drying time and flux comparisons of the various latex blends with the only difference being the carboxyl group content on both of the PS hard and P(BMA/BA) soft latex particles. A trend which can be noted here is that the drying time needed for loss of 99% of the water from the latex increases (Fig. 5A) and the average flux decreases (Fig. 5B) as the amount of carboxyl groups present on both the hard and soft particles increases, indicating

that the carboxyl groups on the latex particles retard the drying rates of the latex blends. Changes in drying conditions influence the drying rates substantially, but do not change the overall trend (compare the two series of samples dried inside the wind tunnel with those dried in air as shown in Fig. 5).
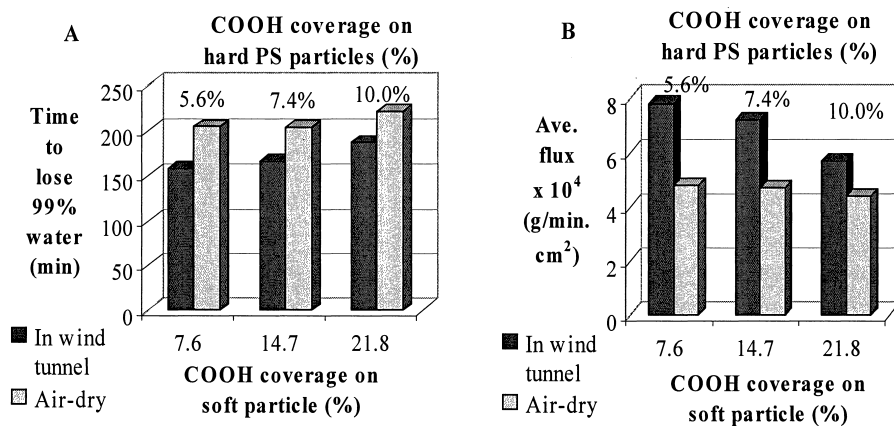


Fig. 5: (A) Drying time needed for 99% water loss from a film, and (B) the average flux vs. the carboxyl group content in both hard and soft latex particles. Wind tunnel conditions: Temp. = 30 °C; R.H. = 25%; A.V. = 50.2 cm/s; Air-drying conditions: Temp. = 20 °C; R.H. = 18%.

Further experiments were carried out to investigate the influence of carboxyl groups that are present only on the P(BMA/BA) soft particles or only on the PS hard particles on the drying rates (Fig. 6); similar results were obtained. Comparison of the time needed to evaporate the same quantity of water from a pool of water to the loss of water from the latex blends (e.g., 99% loss) showed that the pool of water evaporated more quickly than did any of the latex blends. Another feature which was noticed was that the drying rate differences became smaller as the water loss percentage decreased to 50% (Fig. 6). A 50% loss in water occurred in the flat portion of the drying curves seen in Fig. 3B and Fig. 4. This means that the drying rate decrease caused by the presence of carboxyl groups in the edge zone is larger than that found in the uniform wet surface zone. However, the average flux on the uniform wet surface zone also decreases as the carboxyl group concentration increases (Fig. 6).

The effect of carboxyl groups on the decrease of the drying rate could be explained using the following arguments. First, carboxyl groups form hydrogen bonds with the surrounding water molecules and thus decrease the activity of water. Therefore, the partial vapor pressure of water was lowered, and the evaporation rate was decreased. This may be the main reason for the decrease in the average flux which occurred during the early stages of drying. Second, carboxyl groups present at the latex surface could form a network structure somewhat like an interconnected membrane at the edge zone[19]. This structure would decrease the water evaporation rate and might be the main reason for the decrease in the drying rate in the edge zone caused by the presence of carboxyl groups.
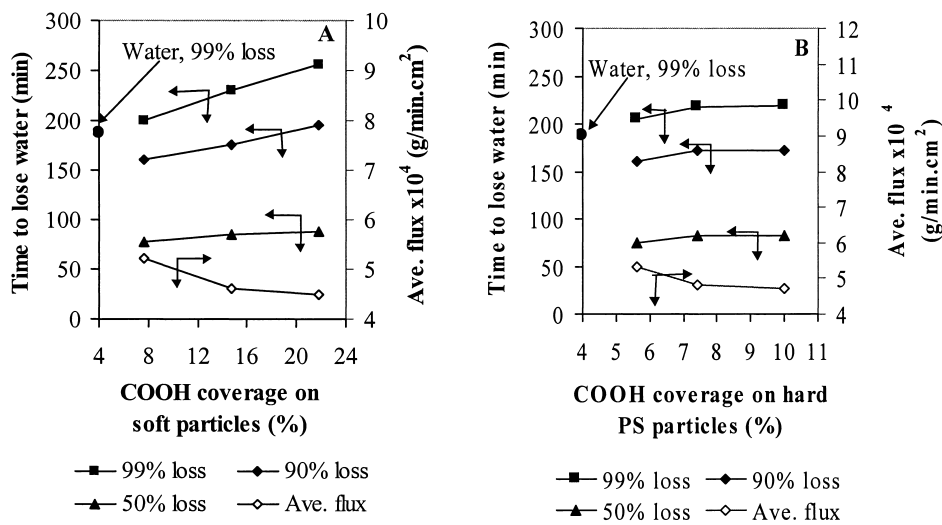


Fig. 6: Comparison of drying times needed for a specific amount (e.g., 99%) of water loss from a film for latex blend dispersions as a function of the content of carboxyl group present: (A) only on the P(BMA/BA) soft latex particles, or (B) only on the PS hard particles. The counterpart latex particles of the latex blends have no carboxyl groups present: Temp.= 30 °C; R.H.= 26%; A.V.= 45.9 cm/s.

## Influence of Neutralization of the Carboxyl Groups on Drying Behavior

To further examine the influence of the carboxyl groups on drying behavior during film formation from latex blends, the carboxyl groups present on the latex particles comprising the latex blends were neutralized by using different bases such as ammonium hydroxide, sodium hydroxide, potassium hydroxide, or cesium hydroxide before the drying experiments were

initiated. The average flux observed over the flat portion of the instantaneous flux vs. drying time curve and the time to lose a specific amount of water were compared between the latex blend samples containing identical initial carboxyl group concentrations neutralized by different bases with different extents of neutralization. Two latex blend systems were investigated: one is the low carboxyl coverage latex blend which consists of P(BMA/BA) soft latex particles with a medium carboxyl coverage (i.e., 21.8% carboxyl coverage on particle surface) and PS latex particles with low carboxyl group coverage (i.e., 10% surface coverage); the other is a high carboxyl coverage latex blend consisting of the same soft latex as was used in the first system and PS hard particles with high carboxyl group coverage (i.e., 77.2% surface coverage). The drying of the above two latex blend systems exhibited quite different responses to the neutralization of the carboxyl groups present in the latex particles.
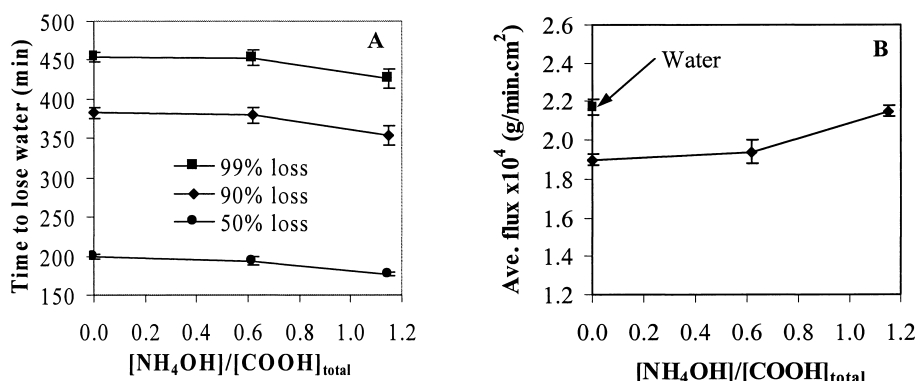
Fig. 7: Drying time and average flux for latex blends with carboxyl groups present as a function of the extent of neutralization of the carboxyl groups by $NH_4OH$: (A) Drying time needed to lose a specific amount of water, and (B) the average flux in the constant drying rate period; Temp.= 23 $^{o}C$; R.H.= 55%; A.V.= 15.2 cm/s.

*Latex Blends Containing PS Latex Particles with Low Carboxyl Group Coverage*

The low carboxyl coverage latex blend was neutralized by weak (ammonium hydroxide) or strong (sodium hydroxide) bases and the influence of the extent of neutralization on the drying behavior of the latex blend was investigated. Fig. 7 shows the influence of the extent of neutralization of the carboxyl groups by ammonium hydroxide on the drying rate of the

carboxylated model latex blend. A slight decrease in drying time (Fig. 7A) and an increase in average flux (Fig. 7B) were both noted as the molar ratio of ammonium hydroxide to carboxyl groups increased, indicating that the neutralization of carboxyl groups by ammonium hydroxide increases the drying rate. These results verify the hypothesis that hydrogen bonding can retard the drying rates of carboxylated latex blends. When the carboxyl groups were neutralized, hydrogen bonding with surrounding water were disrupted, and thus, the drying rate increased as the extent of neutralization increased. It was also found that when the molar ratio of ammonium hydroxide to total carboxyl groups was greater than unity, indicating that there is some free ammonium hydroxide present in the latex blend, this blend dried even faster. It seems that the volatile ammonium hydroxide significantly contributes to the average flux (Fig. 7B).
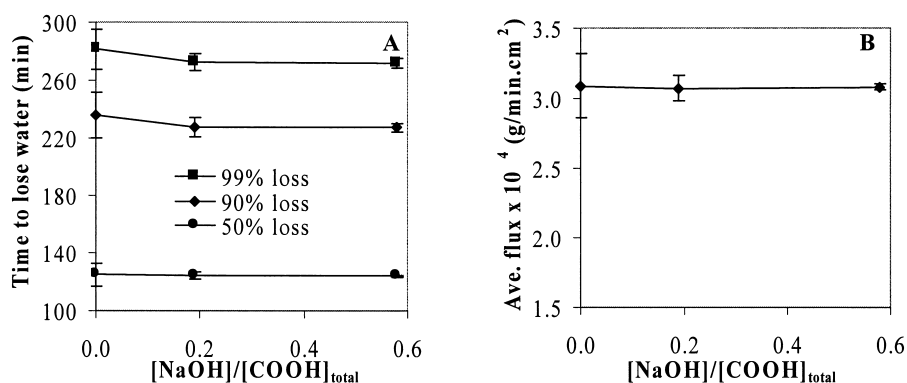


Fig. 8: Drying time and average flux for latex blends with carboxyl groups present as a function of the degree of neutralization of the carboxyl groups by NaOH: (A) Drying time needed to lose a specific amount of water, and (B) the average flux during the constant drying rate period; Temp. = 30 $^{\circ}$C; R.H. = 50%; A.V. = 64.4 cm/s.

When the carboxyl groups were neutralized with sodium hydroxide, the drying time of the carboxylated latex blends decreased as the extent of neutralization of the carboxyl groups increased, while the average flux did not change appreciably (Fig. 8). This indicates that sodium hydroxide has an opposite effect on the drying rate as compared to ammonium hydroxide. On one hand, sodium hydroxide neutralizes the carboxyl groups, resulting in a decrease in the drying rate, which is defined as the neutralization effect here. On the other hand, sodium hydroxide and its salt form will decrease the partial pressure of water[24], and

therefore, decrease the drying rate, which is termed the electrolyte effect. The electrolyte effect is lower in the edge zone because the drying time does decrease as a consequence of neutralization (Fig. 8A).

Table 3: Average flux of the constant drying rate period and the time needed to lose a specific amount of water from the latex blends neutralized by different bases

| Latex blend | Base used | [OH]/ [COOH] | Average flux x $10^4$ (g/min.cm$^2$) | Time to lose 99% water (min) | Time to lose 90% water (min) | Time to lose 50% water (min) |
|---|---|---|---|---|---|---|
| ScBBc15 | None | 0.00 | $1.90 \pm 0.03$ | $453.9 \pm 6.3$ | $382.5 \pm 7.2$ | $199.0 \pm 2.9$ |
| ScBBc13 | NH$_4$OH | 1.15 | $2.15 \pm 0.03$ | $426.0 \pm 12.2$ | $353.0 \pm 12.4$ | $176.8 \pm 1.9$ |
| ScBBc14 | NaOH | 1.19 | $1.84 \pm 0.04$ | $492.3 \pm 2.5$ | $423.8 \pm 3.6$ | $203.8 \pm 4.4$ |

Drying conditions: Temp. = 23 $^o$C; R.H. = 55%; A.V. = 15.2 cm/s.; 21.8% carboxyl coverage on the P(BMA/BA) copolymer soft latex particle surface, 10.0% carboxyl coverage on the PS hard particle surface. All latexes are cleaned, with particle diameters of 120 nm; all blends contain 35 wt.% PS and 65 wt.% P(BMA/BA); solids % of latex blend = 4.0%.

When the carboxyl groups present on the latex particles in a latex blend were neutralized with excess sodium hydroxide, the average flux and drying rate decreased instead of increasing (Table 3). These results were not observed in the latex blends containing carboxyl groups neutralized with ammonium hydroxide (Table 3 and Fig. 7), in which the drying rate continuously increased when the molar ratio of ammonium hydroxide to the carboxyl groups increased in a range higher than 1:1 (e.g., 1.2:1). This further indicated that sodium hydroxide and its salt form would have the effect of decreasing the drying rate (electrolyte effect) as well as exhibiting an effect of increasing the drying rate (neutralization effect). When the molar ratio of sodium hydroxide to the carboxyl groups in a latex blend is larger than unity, the electrolyte effect is stronger than the neutralization effect. Thus, there is a net decrease in drying rate as the molar ratio of sodium hydroxide to the carboxyl groups is higher than unity and, even worse, there is a decrease in the stability of the latex blends. During the drying process of sample ScBBc14 (Table 3) on which the carboxyl groups present were neutralized by sodium hydroxide, obvious coagulation was observed approximately three quarters through the total drying time, while the other latex samples still remained as stable dispersions in the wet film area. However, the latex blends that contain carboxyl groups present in the latex particles, and where the carboxyl groups are neutralized by ammonium hydroxide, show

a net increase in the drying rate as the molar ratio of ammonium hydroxide to the carboxyl groups increases throughout a broad range (from 0 to 1.2; Fig. 7), indicating that the electrolyte effects for ammonium hydroxide are much less than those of sodium hydroxide.

## Latex Blends Containing PS Latex Particles with High Carboxyl Group Coverage

For the high carboxyl group coverage latex blends, the influence of the extent of neutralization of the carboxyl groups on the drying behavior is more complicated than that of the low carboxyl group coverage latex blends. To investigate the influence of the neutralization of these carboxyl groups on the drying behavior of the latex blends, the carboxyl groups present on the latex particles of the high coverage latex blends were neutralized by ammonium hydroxide, sodium hydroxide, potassium hydroxide, or cesium hydroxide under different molar ratios of base to the carboxyl groups.
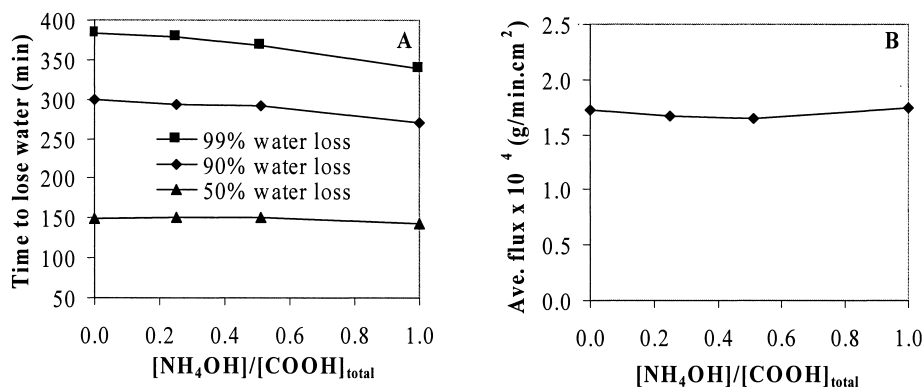


Fig. 9: (A) Drying time, and (B) average flux for latex blends with carboxyl groups present on the particles as a function of the extent of neutralization of these carboxyl groups: latex blends with 77.2% carboxyl coverage on the PS latex particle surface and 21.8% carboxyl coverage on the soft latex particle surface were neutralized by $NH_4OH$; Temp. = 23 $^{\circ}$C, R.H. = 60%, A.V. = 15.2 cm/s.

The influence of the extent of neutralization of the carboxyl groups present on the latex particles by ammonium hydroxide is illustrated in Fig. 9. One can notice from Fig. 9 that the drying time needed to lose a specific amount of water (e.g., 99%, 90%, or 50% of the initial

water) decreased as the extent of the neutralization increased, while the average flux over the flat potion on the flux vs. time curve remains roughly constant. This indicates that the neutralization of the carboxyl groups present on the particles of the high coverage latex blends exhibits opposite effects on the drying rate. Based on the results obtained from the low coverage latex blends, which were described in the above section, we know that one of these effects is the neutralization effect which increases the drying rate, while the other is the electrolyte effect that decreases the drying rate. The results described above also indicated that the electrolyte effect for ammonium hydroxide is less than its neutralization effect. However, the average flux in Fig. 9B did not show any obvious change as the extent of neutralization of the carboxyl groups by ammonium hydroxide increased from 0 to 1.0 which implies that there must be another effect working together with the electrolyte effect to compensate for the neutralization effect. This effect is the formation of clusters.
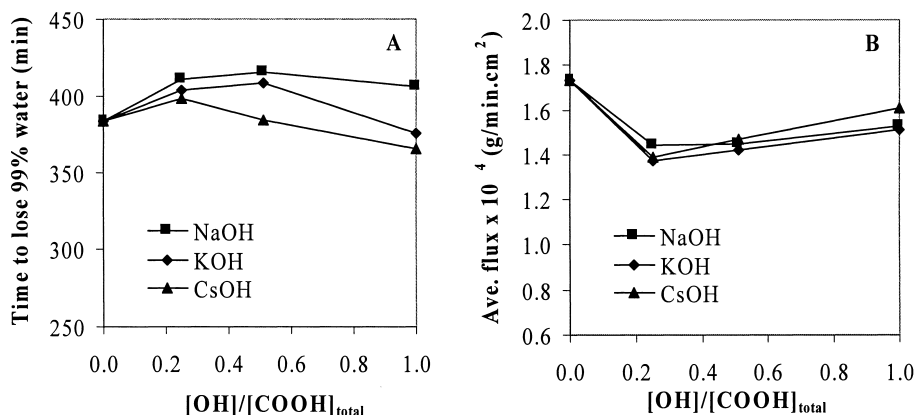


Fig. 10: (A) Drying time and (B) average flux for latex blends with carboxyl groups present as a function of the extent of neutralization of the carboxyl groups: latex blends with 77.2% COOH coverage on the hard PS particle surface and 21.8% COOH coverage on the soft particle surface were neutralized by NaOH, KOH, or CsOH, Temp. = 23 $^{\circ}$C, R.H. = 60%, A.V. = 15.2 cm/s.

When the carboxyl groups present on the latex particles in the high carboxyl coverage latex blends were neutralized by sodium hydroxide, potassium hydroxide, or cesium hydroxide, "abnormal" results were observed. As the extent of neutralization of the carboxyl groups increased, the drying time to lose 99% of the water first increased and then decreased, while the average flux first decreased and then increased (Fig. 10). This phenomenon can no longer

be explained only by neutralization and electrolyte effects. To explain this result, a "cluster" effect is proposed. It may be argued that the high density of carboxyl groups present on the hard PS latex particles form interparticle hydrogen bonds between the carboxyl groups on adjacent PS latex particles, resulting in clustering of the PS latex particles. When the clusters are disrupted, additional carboxyl groups which were initially buried inside the clusters will be released. Thus, a cluster effect would result in a decrease in the drying rate of the latex blends by releasing the buried carboxyl groups and allowing them to be freely hydrated by the surrounding water molecules. The addition of a strong base can disrupt these clusters and release the buried carboxyl groups and, of course, the carboxyl groups released will be neutralized by the base if the amount of the base is high enough. It seems that low extents of neutralization (i.e., low molar ratio of base to the total carboxyl groups present on the latex particles) can release more carboxyl groups than the amount that it can neutralize (Fig. 11).
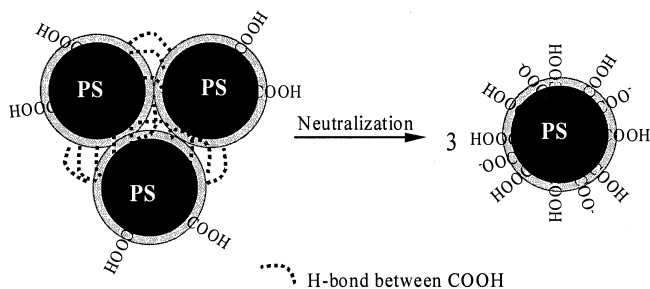


Fig. 11: An example of clusters formed by hydrogen bonds between the carboxyl groups present on the hard PS latex particles and the disruption of the clusters by partial neutralization of these carboxyl groups.

Now the results presented in Fig. 10 can be explained using this mechanism. In the high carboxyl group coverage latex blends, hard PS latex particles form clusters via interparticle hydrogen bonds and most of the carboxyl groups present on the particles are buried inside the clusters. These clusters limited the formation of hydrogen bonds between the carboxyl groups and the surrounding water. Therefore, the un-neutralized high carboxyl group coverage latex blend exhibits a relatively fast drying rate. A low degree of neutralization disrupts the clusters and allows the buried carboxyl groups to be freely hydrated with water. Therefore, the drying rate decreased at a low extent of neutralization for the high coverage latex blends. However, as the degree of neutralization increases further after the clusters are disrupted, the

concentration of freely hydrated carboxyl groups decreases, resulting in an increase in dr
rate (Fig. 10).



|        |        |
|:------:|:------:|
| (A)    | (B)    |

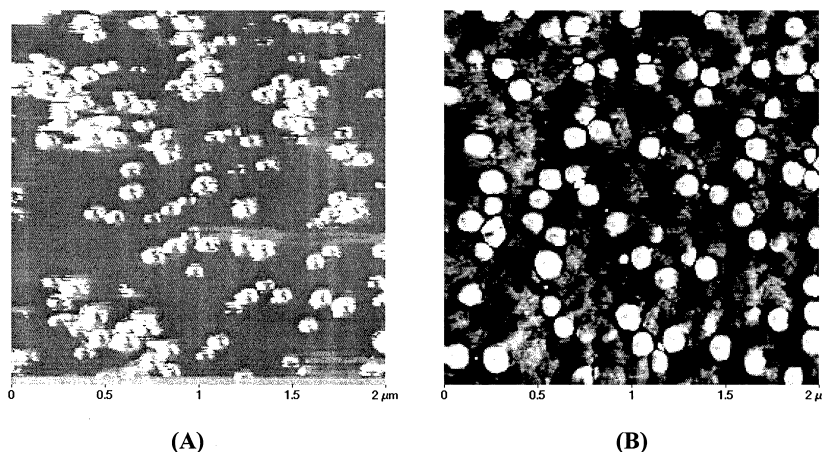Fig. 12: AFM images (phase) of the surfaces of the films cast from the high carboxyl gr
coverage latex blends: (A) the carboxyl groups were not neutralized, and (B) the carb
groups were 100% neutralized by potassium hydroxide.

The clusters consisting of PS latex particles with high carboxyl group coverage and
disruption of these clusters by the neutralization of the carboxyl groups present on
particles were also experimentally observed by atomic force microscope (AFM; 1
Scientific Instruments, BioProbe Electronics Module; Fig. 12). In AFM phase ima
(intermittent-contact mode), the AFM displays images based on the properties of the poly
materials instead of topographical considerations.[25] The latex blend films investigated
consist of PS and P(BMA/BA) polymers. Phase images are better than the topographic im
in observing the distribution of the PS latex particles among the soft matrix on the surfac
the blend films. From Fig. 12, one can note that on the surface of the film cast from a
carboxyl coverage latex blend, there are many large clusters of latex particles and indivi
PS particles are rarely found (Fig. 12A). However, when the carboxyl groups present or
latex particles for the high coverage latex blend were neutralized by a strong base suc
potassium hydroxide, no clusters of PS latex particles can be observed on the surface o
latex blend film (Fig. 12B). These AFM images provide evidence supporting the suppos
that the high densities of carboxyl groups present on PS particles form inter-particle hydro

bonds between the carboxyl groups resulting in the formation of PS particle clusters, and these clusters are disrupted by the neutralization of the carboxyl groups by a strong base.

## Conclusions

The drying process for latex blends consisting of cleaned hard PS and soft P(BMA/BA) latex particles shows a drying edge surrounding the wet latex film. This drying edge moves towards the center of the latex droplet and stops moving at the very late stage of the drying process when the wet film area is very small. The drying rate is not uniform over the entire wet film. Water evaporates much faster from the drying edge zone than it does from the uniform wet film zone. The abnormally fast increase in the instantaneous flux vs. time curve during the late stages of drying is due to an increase of the ratio of the drying edge zone to the entire wet film area which increases very quickly at the late stage of drying. The presence of carboxyl groups on either hard or soft particles or both particles of the model latex blends decreases the drying rate. The influence of the neutralization of the carboxyl groups present on the latex particles on the drying behavior depends on the carboxyl group coverage on the hard PS particles and the properties of the bases used for the neutralization. In the low carboxyl group coverage latex blends, the neutralization of the carboxyl groups present on the latex particles by ammonium hydroxide or sodium hydroxide results in an increase in the drying rate. In the high carboxyl group coverage latex blends, the neutralization of the carboxyl groups by ammonium hydroxide also increases the drying rate. However, neutralization by a strong base such as sodium hydroxide, potassium hydroxide, or cesium hydroxide first decreases and then increases the drying rate as the extent of neutralization increases. The "abnormal" drying behavior could be explained by a "cluster" effect. PS latex particles with high surface coverage of carboxyl groups form clusters via hydrogen bonding between the carboxyl groups on adjacent latex particles and these cluster are disrupted by the neutralization of these carboxyl groups by a strong base. A low extent of neutralization disrupts the clusters and releases additional carboxyl groups than the amount the base is able to neutralize, resulting in a decrease in the drying rate. Further addition of strong base neutralizes the released carboxyl groups and, thus, increases the drying rate at high extents of neutralization.

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