Film Formation of Monodispersed Polystyrene Latex at High Temperature

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ABSTRACT: This report discusses the drying behavior of monodispersed polystyrene latex at elevating temperature with particular attention to the relationship between water evaporation rate and morphological evolution during the film formation process. At the first stage, water evaporation rate was less influenced by the skin film formed at the latex/air interface, which was consistent with Croll's model. During this stage, a drying front advanced from the top film toward the bulk dispersion. At the final stage of film formation, the water evaporation rate was less than that of the initial stage, and another drying front developed from the interior region outside the system. Two distinct boundaries corresponding to the opposite directions of the second drying front between completely dried region and wet region were found if the film was peeled off the container surface. Besides, some particular morphologies were found in the completely dried region, which was likely related to preferable coalescence among the particles induced by capillary force because of water evaporation. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1835–1840, 2001

Key words: monodispersed polystyrene latex; film formation, high temperature; morphology; drying front

INTRODUCTION

Up to today especially, when environmental and ecological requirements have become increasingly stringent, polymer latexes with small (or zero) amount of volatile organic compounds have re-ceived more and more attention because of their diversity of application and lack of pollution to the environment. Better performance could be expected to achieve from monodispersed latexes by their maximum closely stacking. More recently, the study on monodispersed latexes as models to mimic the relationship between interaction and stacking of particles commonly encountered in condensed matter physics has become a popular subject.[1,2] On one hand, the knowledge about latex packing during the film formation process helps in understanding how atoms stack into bulk materials and its relationship with interaction potential among them. On the other hand, it also serves to design latexes so as to achieve latex films with desired performance.

Some models[3–5] have been proposed, including those of Vanderhoff, Croll, and Wang and Winnik. Vanderhoff[8] thought that three stages existed during the film formation process. In the first stage, particles are randomly mobile in the bulk dispersion and water evaporates from the free surface by a constant rate essentially the same as that of pure water. The second stage is corresponding to particles' irreversible contact losing their mobility and water evaporation rate decreases to one tenth or less of the initial rate, which is attributed to reduced surface areas being available for water evaporation. In the final stage, polymer chains diffuse across the interface between the deformed latexes.

Later, Croll[4] proposed a two-stage model. During the first drying stage, water evaporation occurs from a surface that retreats through the film as drying progresses, and a dry and porous upper film layer is obtained. The wet layer as a reservoir of water contacting the substrate supplies water to maintain a constant evaporation rate. During this stage, water percolates through the drying film. At the onset point of the second stage, water evaporation rate begins to drop when the wet region is depleted with the boundary zone contacting the substrate. During this stage, the thickness of the transition zone decreases until all the water evaporates and the film is dry. However, Croll's model lacks the description about the residual diffusion of water at very low water concentration.

Wang and Winnik[5] gave much attention to the investigation of polymer chains across the interfaces between the deformed latexes via the nonradiation energy transferring technique.

Besides these, some other comprehensive models[6,7] have been proposed. According to these models, two drying fronts are emphasized. The first drying front corresponds to phase transition from latex random distribution in the bulk dispersions to ordered packing, and the second corresponds to continuous phase inversion from water (or air) to polymer matrix.

Although many models have been proposed to study the film formation process, it should be noted that thickness of the studied film was very thin and the study was performed at relatively low temperatures. This means that almost all studies were performed under a nearly equilibrium condition. Here, we are concerned with what will happen if the film is relatively thicker and water evaporation rate is faster at high temperature, e.g., under nonequilibrium conditions.

EXPERIMENTAL

Preparation of Monodisperse Polystyrene Latex

Monodisperse polystyrene latexes were prepared by one shot emulsion polymerization and the ionic emulsifier (Emulgator NPS25, a gift from BASF A. G.) was used instead of sodium dodecyl sulphate.[8] The final dispersions were filtered through a 100-mesh grid to remove the grit formed during the polymerization. Particle size and its distribution were determined by scanning electron microscopic (SEM) observation. Monodispersity of the emulsion was verified by the iridescent color effect while drying it.

Procedure of Film Formation

Approximately 4 g of dispersion was added into a glass bottle about 35 mm in diameter and 23 mm in height, and then loaded in an oven at 95°C. The skin film formation was monitored through visualization observation. Water evaporation rate was determined by a commonly used weight loss method.[6] It should be pointed out that container edge effects were neglected in this study because the free surface for water evaporation was large and the sample selected in the center region of the film was used to study the morphology.

Characterization

The skin film formed during the first stage of film formation process was stripped off the dispersion and dried in vacuum under ambient conditions. Au was sputtered on the dried skin film and the morphology was observed with SEM. The completely dried film was fractured under ambient conditions and sputtered with Au in vacuum. The morphological profile of the fracture was also observed with SEM. The scanning electron microscope used in this study was a Hitachi (Japan) SEM (S-530).
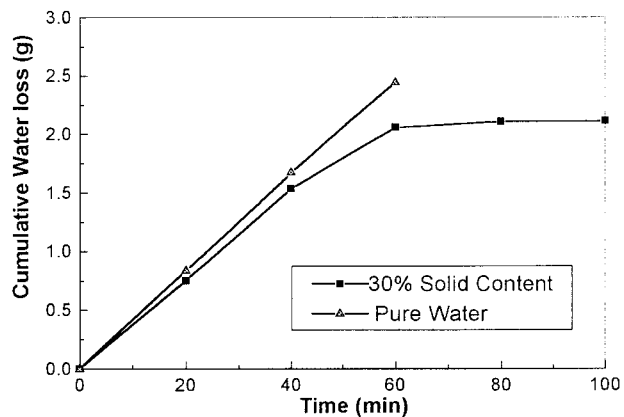
RESULTS AND DISCUSSION

Water Evaporation Rate

Figure 1 shows the effect of crosslinking degree of the latexes on water evaporation rate. From the curves, it can be seen that water evaporation is composed of two representative stages: an initial constant rate stage and another constant stage but with much lower rate. The former one is al-
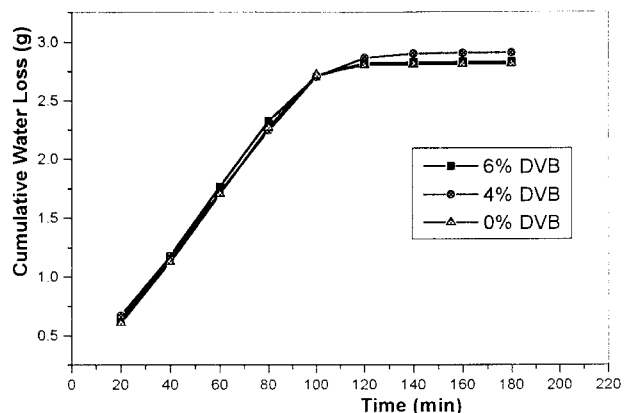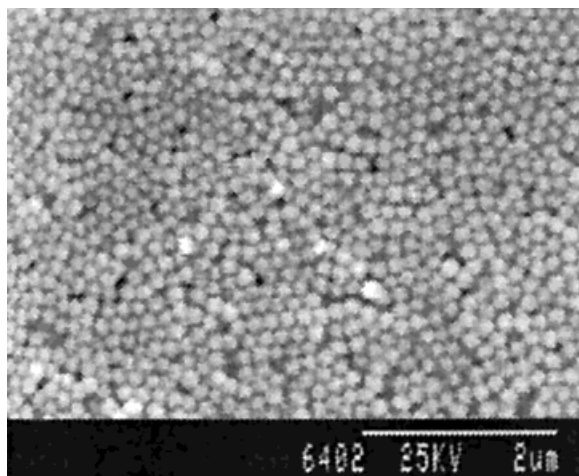
Figure 1 Dependence of water evaporation rate on crosslinking degree.

Figure 3 Scanning electron micrograph of the top wet skin film.

most the same as that of pure water, as shown in Figure 2. This stage is corresponding to phase transition from randomly mobile motion of the particles to the irreversible contact among the particles. It should be noted that the voids among the particles are filled with water. The estimated water volume fraction at the deflection point of the curves is about 80%. This value is slightly higher than 74% corresponding to the case of maximum close packing of monodispersed particles. This is mainly because of the stacking defects of the particles especially in the case of faster water evaporation rate at higher temperature. The rate of water loss in the initial part of the second stage is more representative of diffusion through capillary channels in the film than that through the polymer itself. However, as film drying and further gradual coalescence processes slowly proceed, the rate slowly approaches that

**Figure 2** Comparison of water evaporation rates of dispersion and pure water.

representative of the polymer. It is reasonable to deduce that water diffusion through the polymer becomes the predominant mechanism, when the further gradual coalescence is completed eventually, which has been confirmed.[4] This is corresponding to the final part of the second stage.

Moreover, it can be seen that water evaporation rate is less influenced by the crosslinking degree of the latexes with altering content of divinyl benzene (DVB). It is emphasized that all measurements were undertaken after the thin iridescent skin film was formed at air/dispersion interface. From the aforementioned discussion, it is shown that water evaporation rate is less influenced by this skin film, which is almost the same as that of pure water. This fact is inconsistent with Vanderhoff's model. According to Vanderhoff, the initial constant water evaporation region is corresponding to Brownian motion of latex without the formation of the skin film, and water evaporation rate will become slower upon the formation of the skin film. In fact, during the stage that an iridescent skin film was visually observed in this study, water evaporated at a constant rate almost the same as that of pure water. This fact agrees with Croll's model. It is possibly ascribed to the formation of some holes and cracks within the film as the pathways to allow water evaporation at a constant rate, which is confirmed by the morphology as shown in Figure 3.

In the first linear stage, a boundary layer between the as-formed skin film and the bulk dispersion proceeds from the top surface to the bottom surface. At the deflection of the curve, the
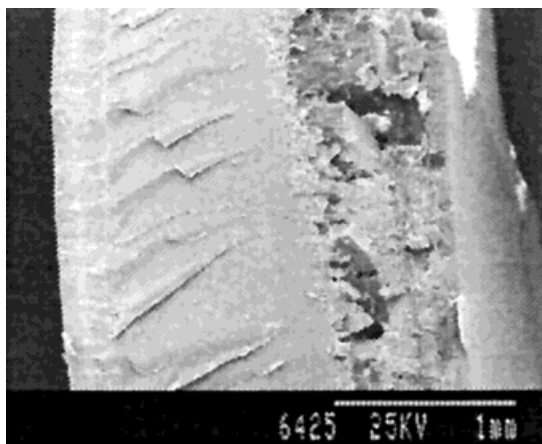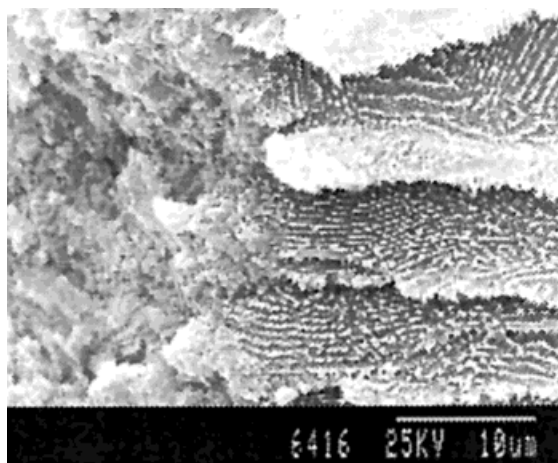
Figure 4 Scanning electron micrograph of the dried film (the left: top surface, the right: bottom surfaces).

Figure 5 Scanning electron micrograph of the left boundary as in Figure 4.

drying front impinges on the container bottom. This is corresponding to the onset when the film became completely dried. If the film strongly adheres to the container bottom, this complete drying process proceeds from the bottom to the top surface. During this course, the stabilization of the surfactant molecules becomes weak in the absence of water and the latexes become coalesced if the experimental temperature is above minimum film formation temperature. It is noted that deformation and coalescence among the latexes are promoted by capillary forces originated from water flowing within the channels. The force is approximately perpendicular to the water flow direction. Therefore, it is explained by the existence of preferable coalescence among the particles perpendicular to the film surface because water motion direction is perpendicular to the film surface.

If the film peels from the container bottom surface at the deflection of water evaporation rate curve, there exist two directions for the residual water to evaporate, toward the top film surface with higher rate and the bottom film surface with slower rate. In this case, the second drying front starts from the inner region of the film rather than the film bottom surface. Two drying fronts will be derived from the second drying front and advance along opposite directions with varied velocities.

SEM Observation of the Film Morphological Evolution

Figure 3 shows the morphology of the wet skin film. It can be seen that there exist polycrystal domains formed by highly ordered stacking by the latexes leaving some defects such as holes and cracks located at the crystal boundaries. These defects act as channels to ensure water evaporation at a constant rate through the skin film.

Figures 4–9 show the morphological profiles along the fracture of the dried film. It is noted that the film is peeled from the container bottom surface. As analyzed above, two drying fronts are expected to advance along two opposite directions with varied velocities.

Figure 4 shows a profile of the whole fracture, in which the left side is corresponding to the top surface of the film. It is found that there exist two white boundaries with varied depths close to the two film surfaces. The boundary at the left side is near the top film surfaces, whereas the other one
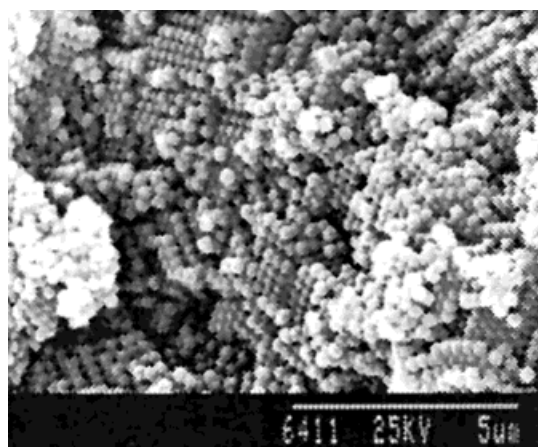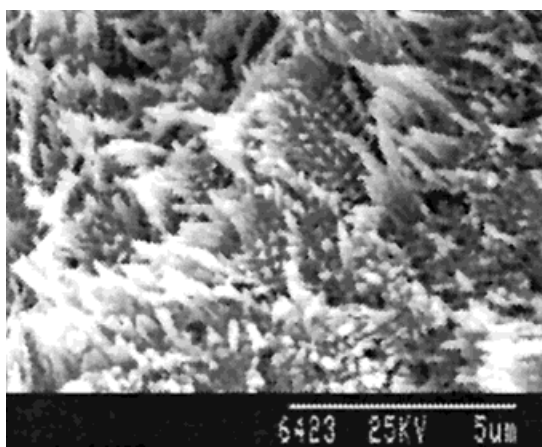

Figure 6 Scanning electron micrograph of the left region as in Figure 4.
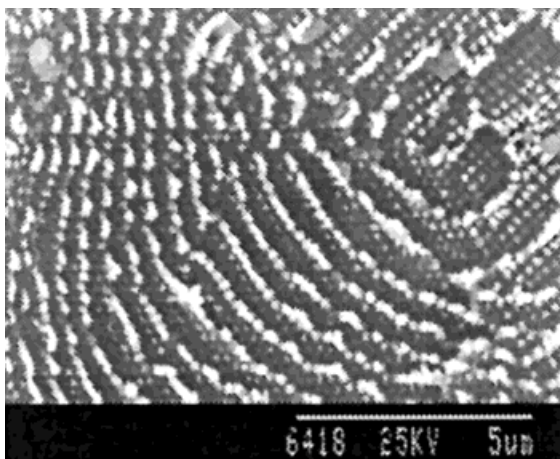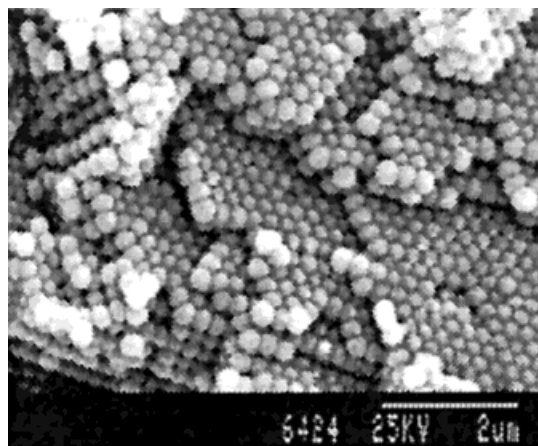
Figure 7 Scanning electron micrograph of the left middle region.

Figure 9 Scanning electron micrograph of the right region.

is far away from the bottom film surfaces. This means that the drying front advances faster upward to the upper side of the film rather than downward to the bottom side of the film. Visualization observation indicates that the region between the two boundaries is transparent, whereas the other regions are turbid. Figure 5 clearly shows that there exists a transition region between the turbid regions and the transparent region. Figure 6 shows the morphology of the top turbid region. It can be seen that the particles remained spherical shape memorized rather than coalesced. While in the transparent region as shown in Figure 7, the latexes have already well coalesced into continuous film. In some transparent region as shown in Figure 8, it is found that the particles coalesced preferably within the

plane parallel to the film surface. There exist fibril structures in this region, which correspond to the strings formed by the coalesced latexes within the plane just like biaxial elongation. This is likely induced by capillary force parallel to the film surface originated from the water evaporation direction perpendicular to the film surface.

Figure 9 shows an SEM image of the backside region of the film. It is found that the morphology is almost the same as that in Figure 5. This implies that the latexes in this region are not completely dried.

CONCLUSIONS

Film formation process of monodispersed polystyrene latex was investigated, including water evaporation rate as well as the morphological evolution at elevating temperature. It is shown that water evaporation rate is less influenced at the beginning stage of film formation in the linear region of the water evaporation curves even after a skin film has formed at the air/dispersion interface. There exist many holes and cracks within the film to permit water evaporation thereby, which is consistent with Croll's model.

SEM observation of the dried film shows that there exist two boundaries located in the vicinity of the two film surfaces. In the middle region, the film is transparent and the latexes have well coalesced. Beyond this region, the film is turbid and the particles remain a spherical structure. The two boundaries correspond to the two water evaporation directions.

Figure 8 Scanning electron micrograph of the middle region.

At the beginning stage when the particles start to be at maximum closely stacked, the first drying front advances from the top film surface toward the bulk dispersion. At the deflection of water evaporation curve, the first drying front impinges on the container bottom surface and the whole system becomes immobile. Afterward, a second drying front advances from the bulk system to the film free surface, until the whole system becomes transparent. This process is characteristic of the coalescence among the latexes above film formation minimum temperature. Therefore, the film is apparently dried from outside toward inside the bulk dispersion, and it is completely dried from inside toward outside.

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