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Latex film formation studied with the atomic force microscope: Influence of aging and annealing

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Abstract: The surface structure of latex dispersion films was examined with an atomic force microscope. All measurements were done in air on latex films having a minimum film formation temperature of 12 °C and a glass transition temperature of 18 °C. One aim of this study was to follow structural changes during film formation. Three minutes after spreading the film, its surface layer dried. Afterwards, the structure of the film did not change anymore. Only after 4 months could structural changes be observed: Though individual latex particles could be identified, the particles partly melted into one another.

After annealing films at 50° or 60 °C for 4 h, the latex particles partly melted into one another, but individual particles could still be identified. When annealing at or above 80 °C, no individual latex particles were visible anymore. With increasing temperature the film roughness decreased from 3 nm without annealing to 0.8 nm at 100 °C annealing temperature. In addition, islands of 2–4 nm thickness appeared on the film surface. These islands could be scraped off the film by increasing the force between tip and sample, indicating that they are composed of surfactant which was squeezed out of the film.

Key words: AFM – atomic force microscopy – latex dispersions – polymer films – latex particles

Introduction

Latex dispersions are commonly used in paint, paper, adhesive, and coating industries where the properties of the film are of great importance. They consist of polymer particles dispersed in an aqueous medium often stabilized by surfactants or protective colloids to prevent flocculation. When cast onto a substrate, water evaporates and a continuous clear film forms if the application temperature is above the minimum film formation temperature (MFT). The mechanism of film formation is generally considered to be divided into three phases: Concentration, deformation, and coalescence plus interdiffusion of the latex particles [1]. The nascent film is normally weak. Its mechanical properties, such as tensile strength, improve gradually, often requiring days or weeks to reach their final properties [2]. It is commonly believed that the enhancement of tensile strength is a consequence of polymer diffusion across the particle-particle interface in the film [3–7]. Important factors responsible for interdiffusion capability of polymers in latexes are the molecular weight of the polymer, the temperature at which the film is formed, the spatial distribution of chain ends near the interface [8], and the steric and electrostatic stabilization of the latex [9]. Different techniques like small-angle neutron scattering (SANS) [8, 10–12], freeze fracture replication transmission electron microscopy [13], and atomic force microscopy [14–16] have been applied to investigate the morphology of latex dispersion films.

For this paper, we examined latex dispersion films with an atomic force microscope (AFM) [17, 18]. With the AFM topographic images of the film surface can be obtained at high resolution without destroying or deforming the film. Imaging can be done in air without taking special care for dust-free environment. No special preparation is needed and the films do not have to be exposed to vacuum. This study deals with two objectives. First, we intended to find out at what time-scale structural changes take place at the film surface. Second, the influence of annealing on the surface structure was investigated.

Materials and methods

Latex and film preparation

Films were prepared from a poly(methyl methacrylate/butyl acrylate) latex, whose preparation followed standard procedures [19, 20]: A monomer emulsion (ME) was prepared by a mixture of 600 g water, 7.5 g sodiumdodecylsulfate (SDS), 4.5 g $Na_2S_2O_8$ (APS), 15 g methacrylic acid, 750 g methyl methacrylate and 750 g butyl acrylate. In a 4 l vessel fitted with a stirrer and a reflux condenser a mixture of 820 g water, 3.75 g SDS and 60 g ME were heated up to 83 °C. After an initiation period of about 5 min a mixture of 0.68 g APS in 20 g water was added at once and the remaining ME was fed at 83 °C over a period of 210 min. Afterwards, the latex was kept at 83 °C for 1 h and then cooled down to room temperature and adjusted to pH 9 by adding 30 ml of 12.5% ammonia solution. Films prepared from the latex (solid contend 50.7%) had a minimum film formation temperature of 12 °C and a glass transition temperature of 18 °C, as determined by differential scanning calorimetry. The mean particle diameter (d_w) measured by dynamic light scattering (Zeta Auto-Sizer IIc) was 120 nm with a polydispersity d_w/d_n of 1.1. The latex was cast on microscope slides with a wet film thickness of 100 μm, leading to a thickness of the dry film of about 50 μm. Then, they were annealed at room temperature, at 50°, 60°, 80° or 100 °C for 4 h. After this period, films were stored at room temperature. All films were clear and free of cracks.

Atomic force microscope

All images were taken with a NanoScope II Instrument (Digital Instruments Inc., Santa Barbara, California) in constant force mode. They display the topography of the sample. We used silicon nitride cantilevers of 100 μm or 200 μm length (0.094 N/m or 0.022 N/m spring constant) with integrated, sharpened tips (Olympus Opt. Ltd., Tokyo). A laser beam was focused onto the backside of the gold-coated cantilever. By measuring the position of the reflected beam, the reflection angle and, consequently, the deflection of the cantilever was measured.

The scanner was capable of scanning a region of 12 μm by 12 μm. It was calibrated laterally with images of mica and vertically with purple membranes and an inclined plane as described previously [21]. All AFM measurements were done in air at room temperature. A typical force between tip and sample was 10 nN. It took between 20 and 72 s to record one image. From all images the best-fit base plane was subtracted to remove the average tilt. Some images were low-pass filtered.

To avoid artifacts due to friction between tip and sample, it was always made sure that the back-and-forth scans were similar, except for a small hysteresis. In some cases, however, we intentionally used friction as image contrast. Friction twists the cantilever while scanning (Fig. 1). Depending on the scan direction, this twist changes the height signal [22]. When scanning perpendicular to the plane defined by the incoming and the reflected laser beam, friction effects are negligible. When scanning in parallel to the plane defined by the laser beams, friction effects increase (in one direction) or decrease (in the opposite direction) the apparent height, With some tips friction effects can dominate the image. This can be checked by comparing the back-and-forth scans.

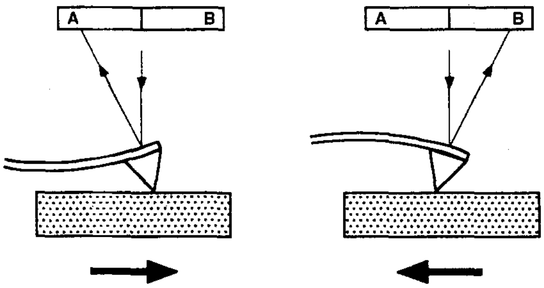

Fig. 1. When scanning parallel to the axis of the light beam, friction contributes to the image contrast. Friction twists the cantilever. As a result, the light beam is deflected differently and the photodiodes A and B measure a different position of the reflected beam

Unfortunately, we were not able to work in friction mode systematically and quantitatively, since only a few tips showed significant friction effects.

Surface roughnesses were calculated from

$$\sigma = \sqrt{\frac{1}{n} \cdot \sum_{i=1}^{n} (z_i - Z_i)^2}\,,$$

where z_i is the observed height at a certain point i, z_i is the best-fit base plane at the point i, and n is the total number of data points in one image. The surface roughness was determined over areas of 1–4 μm^2.

Results and Discussion

Figure 2a shows a typical surface of latex dispersion film in topview. Latex particles had a spherical shape. Sometimes the latex particles formed hexagons. However, hexagonally close-packed regions seldom extended over more than few latex particles in one direction. No long range order was observed. Ordering was lower than in dispersion films imaged by Wang et al. [14] and Juhué and Lang [15]. A possible explanation is that our films were thicker (50 μm) than the films imaged by these authors (2–20 μm). It is also possible that the size distribution of our latex particles was broader or that the surfactant played a role.

Despite a film thickness of about 50 μm, the roughness of latex dispersion films was only about 3 nm – less than 0.01% of the thickness (Fig. 2b). A possible explanation for this surprisingly low film thickness is that surface tension plays an important role during film formation. In order to minimize the total surface energy at the air/latex solution interface, the interfacial area is reduced. Consequently, the roughness is reduced and protrusions are avoided.

In order to image film formation, we spread latex on microscope cover glasses on top of the AFM scanner. After spreading the film it took about 50 s to mount the AFM head onto the sample and to be ready to image. Imaging, however, can only be done on solid surfaces. For this reason, it was impossible to obtain images while the film was still liquid. A further problem occurred when the tip was dipped into the liquid latex solution. Then, it was often contaminated and became useless; at the least, it had to be cleaned and a new experiment had to be started. Therefore, we did experiments with different delay intervals between film spreading and tip engagement. After 160 to 230 s the upper surface layer dried. In one fortunate case an image was taken while the surface layer of the latex dispersion film became solid (Fig. 3). In the lower half of Fig. 3 the dispersion film was still liquid. Then, within less than 1 s, the surface layer dried and individual latex particles became visible. This structure was stable and did not change anymore.

Figure 4 shows the same spot on the dispersion film as that in Fig. 3. It was imaged 11 min after Fig. 3. The tip had disturbed film formation in the bottom center part of the image. This supports the idea that the film was still liquid when the tip

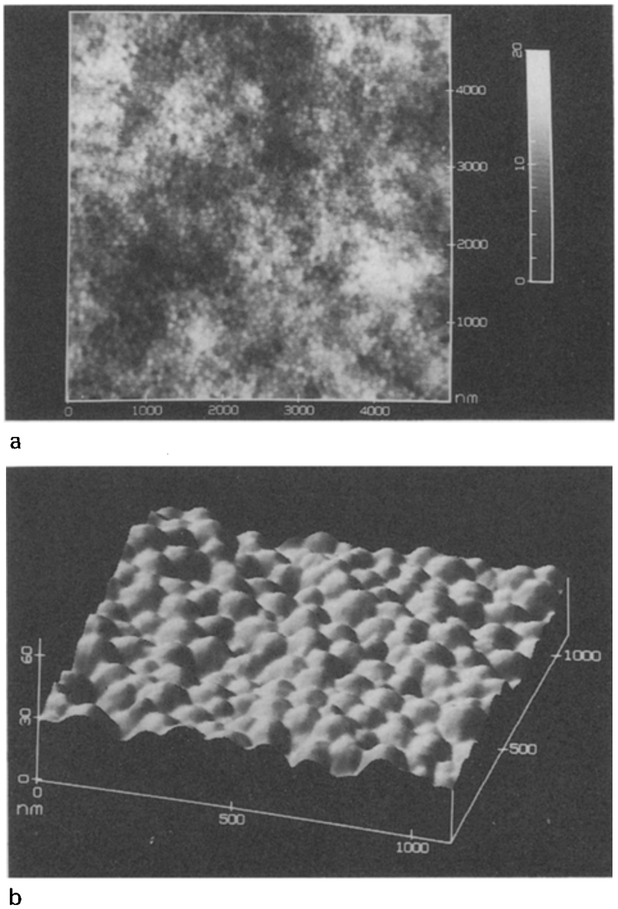

Fig. 2. Top view (a) and surface plot (b) of a latex dispersion film. Scan sizes are indicated in nanometers. The films were 1 and 3 days old, respectively. They were formed at room temperature

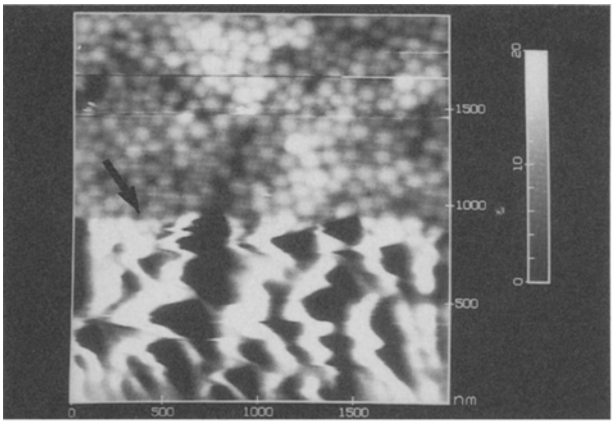

Fig. 3. Formation of a latex film. The image was taken 3 min after applying the solution to a glass slide. It was scanned from bottom to top in 20 s. In the bottom part, that is during the first 9 s, the film is still liquid. Then, as indicated by an arrow, the film became solid. In the top half a change in the contrast can be seen. This is probably due to the fact that the tip picked something up during film formation, which is lost again at this point

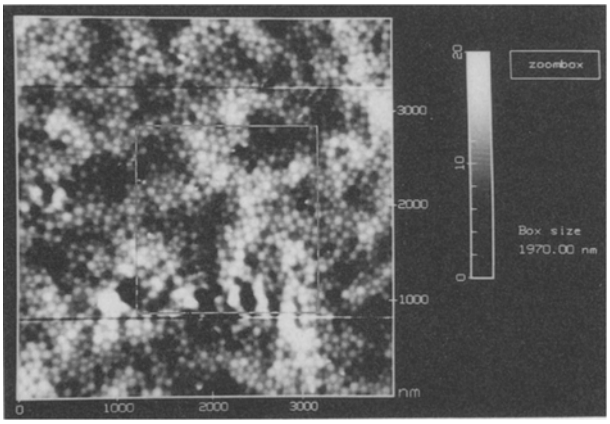

Fig. 4. The same place on the sample as shown in Fig. 3 showing a larger area. A square indicates the area scanned before. The image was taken 11 min after Fig. 3

engaged. All latex particles observed seconds after film formation (top half of Fig. 3) are still at the same position after 11 min. Hence, the film was stable about 3 min after spreading and no significant changes occurred anymore.

Figure 5a shows the topography of a latex dispersion film after 9 days. No significant difference to films being only a few minutes old are visible. In friction mode (Fig. 5b) an additional feature can be seen: A narrow region of material with a different friction coefficient appeared at some places between the latex particles. This material must be thinner than about 1 nm, otherwise we would have identified it in the topographic image. These narrow regions can only be composed of surfactant which was squeezed out of the film during film formation.

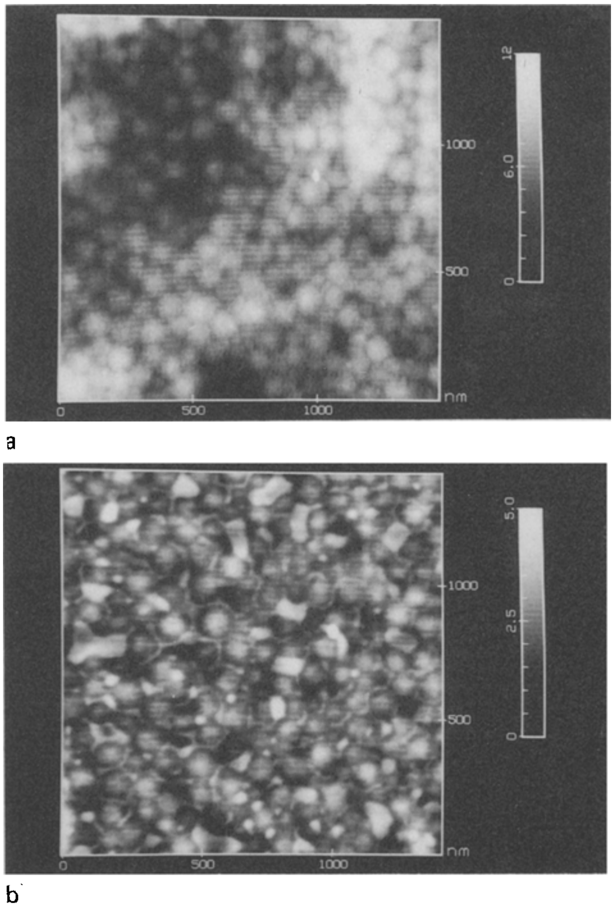

Fig. 5. Typical latex dispersion film 9 days after formation kept at room temperature. In (a) the topography of the film is shown; (b) shows exactly the same area using mainly friction as image contrast. Regions of low friction appear light, regions of high friction dark. Changing the contrast from topography to friction was done by rotating the scan direction by 90°

Latex dispersion films were unaltered even after several weeks. Only after storing them for 4 months at temperatures between 21° and 28 °C did significant changes occur (Fig. 6). After 4 months individual latex particles could still be identified but the particles partly melted into one another. The roughness of the surface was also reduced from typically 3 nm just after film formation to 1 nm after 4 months.

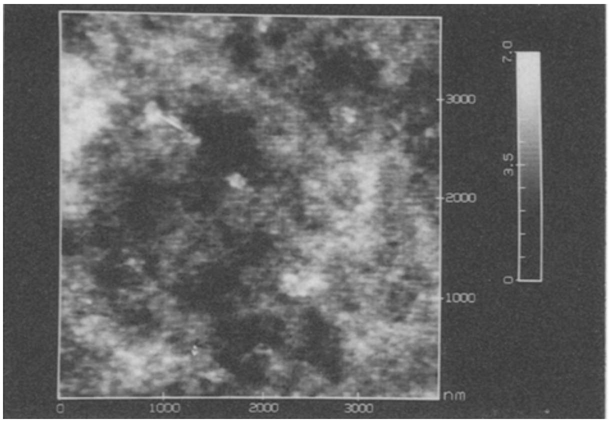

Fig. 6. Latex dispersion film 4 months after formation stored at room temperature

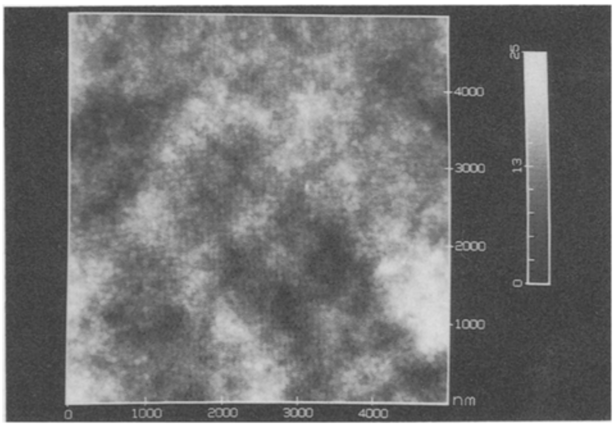

Fig. 7. Latex dispersion film annealed at 50 °C for 4 h

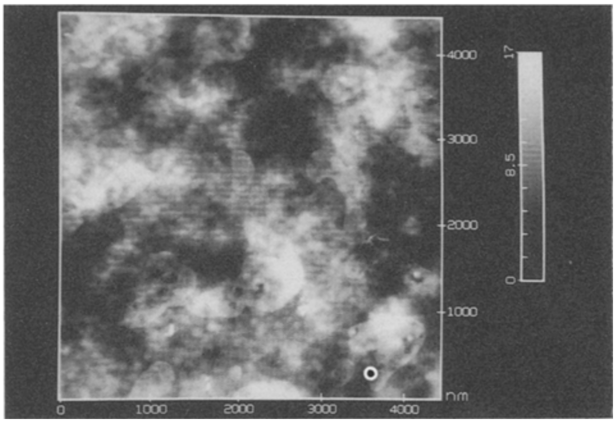

Fig. 8. Latex dispersion film annealed at 60 °C for 4 h

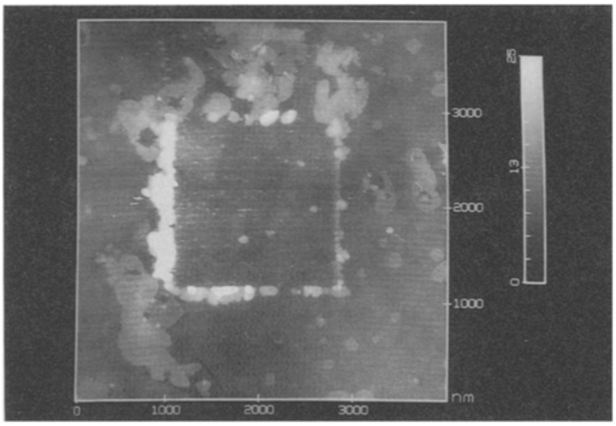

Fig. 9. Latex dispersion film annealed at 80 °C for 4 h. The top layer in the center square was scraped off by scanning the surface a few times with an increased force of about 30 nN

An important question concerning film formation is how far the polymer chains interdiffuse across the latex particle boundaries. With the AFM no direct answer to this question is possible since it cannot trace individual polymer molecules. However, the topography of the films being 4 months old strongly indicates that particles at the surface were not only deformed but melted into one another.

In another series of experiments latex dispersion films were annealed after film formation at 50°, 60°, 80° or 100 °C for 4 h. These films were imaged within 5 weeks after formation and annealing. Films which were only exposed to room temperature are already shown in Figs. 2 to 5. After annealing at 50 °C (Fig. 7) or 60 °C (Fig. 8), the latex particles started to melt into one another, but individual particles could still be identified. The surface roughness decreased slightly from 3.0 nm to 2.5 nm. Islands of 2 to 3 nm thickness covered part of the surface.

Individual particles could hardly or not at all be identified on films annealed at 80 °C (Fig. 9) or 100 °C (Fig. 10). The surface could be described as a relatively smooth plane partly covered by a layer of 2 to 4 nm thickness and with occasional holes of 2 to 3 nm depth. The top layer could be scratched away with the tip by scanning several times with an increased force of about 30 nN (Fig. 9). This produced an uncovered surface. The roughness of the uncovered, pure surface was 0.8 nm at both 80 °C and 100 °C annealing temperature. We did not see significant differences between films annealed at 80° and 100 °C. Differences in the film surfaces shown in Figs. 9

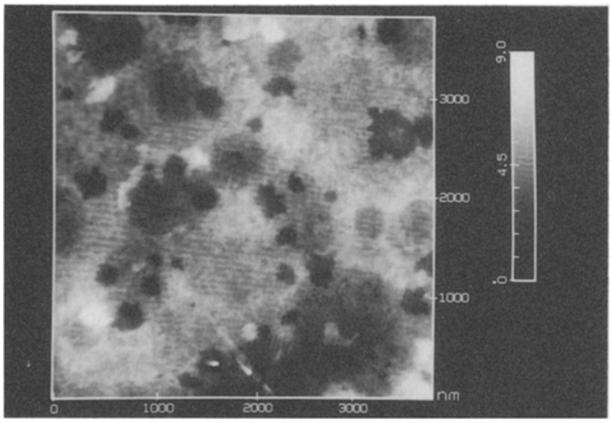

Fig. 10. Latex dispersion film annealed at 100 °C for 4 h

and 10 reflect the inhomogenity of different areas on a sample or between different samples.

Our results differ slightly from the observations of Wang et al. [14]. Wang et al. imaged a latex dispersion film containing particles of 337 nm diameter. The main effect of annealing their films at 70 °C (MFT was 22–25 °C) was the appearance of small holes in the surface. No melting was observed. In contrast, we saw no significant change in the number of holes, but annealing led to melting of the particles into one another.

Conclusion

The surface layer of latex dispersion films dried within 3 min after spreading the film. After this initial drying the structure of the film surface and the relative positions of individual latex particles at the surface did not change for weeks. Only after 4 months could structural changes be observed. Although individual latex particles could still be identified, the particles partly melted into one another.

Annealing films for 4 h at 50° or 60 °C, e.g., 30° or 40 °C above the glass transition temperature T_g, caused the latex particles to partly melt into one another. However, the particles could still be distinguished. When annealing at temperatures at or above 80 °C (60 °C above T_g) no individual latex particles were visible anymore. Film roughness decreased form 3 nm without annealing to 0.8 nm at 100 °C. In addition, islands of 2–4 nm thickness appeared on the film surface. This layer could be scrapped off the film by increasing the force between tip and sample, indicating that it was composed of surfactant which was squeezed out of the film during annealing.

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