

Annealing Effects on the Surface Structure of Latex Films Studied by Atomic Force Microscopy

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The effect of annealing on latex film surface structure was followed by atomic force microscopy. The films were prepared from poly(butyl methacrylate) particles (PBMA, $d = 337$ nm) prepared by surfactant-free emulsion polymerization. The film surfaces were highly ordered, consistent with face-centered cubic packing in the film interior, and each particle maintained a truncated spherical shape. The peak-to-valley distance Δz was monitored as a function of annealing time. From Δz , the remaining surface per particle was calculated. With the aid of a simple diffusion model, we conclude from these data that polymer chains near the latex surface diffuse much faster than those within the film.

When films are formed from aqueous dispersions of soft latex particles, the spherical polymer droplets are deformed to space filling polyhedra under the influence of osmotic and surface forces that accompany drying of the film.¹ At low ionic strength and in the absence of surfactant, the particles become ordered in the liquid state. The face-centered-cubic (fcc) packing persists as the film dries.^{2,3} Recent freeze fracture (FFTEM)^{4,5} and ordinary transmission electron microscopy (TEM)³ studies show that under these circumstances, the particles in the interior of the film deform to essentially perfect rhombic dodecahedra.

This distortion of fcc-packed spheres into regular polyhedra implies that the forces driving the deformation in the interior of the film operate isotropically. The situation should be very different at the surface of the film. Micrographs of latex film surfaces, obtained using a shadowing technique in the preparation of a platinum replica of the surface, show that latex particles in the film surface maintain a truncated spherical shape.⁶ As these films are annealed, one expects the periodic surface structure of the film gradually to fade.

Atomic force microscopy (AFM)^{7,8} is an ideal technique for studying the evolution of surface structure in latex films. Its resolution is comparable to, or exceeds, that available by scanning or transmission electron microscopy. Since the samples require no special surface treatment, and the technique is nondestructive, film samples can be examined, annealed, and reexamined many times. This brings the measurement much closer to the annealing experiment.

Here we report a brief study of the effect of annealing on the surface of poly(butyl methacrylate) (PBMA) latex films. These films were prepared by a simple casting technique, onto atomically smooth mica substrates, using

a surfactant-free dispersion (37 wt % solids) of 337-nm PBMA particles with a very narrow size distribution. These particles order in the aqueous phase and the ordered structure persists throughout the drying process to give an fcc arrangement of particles within the film. Since we have previously reported the effects of annealing on the internal film morphology for the same latex sample, we are able to compare the evolution of surface morphology over time with that of the film interior.

Experimental Section

The latex sample employed here is identical to that described in refs 4 and 8. The particles are narrowly distributed in size with a mean diameter of 337 nm. They were prepared by surfactant-free emulsion polymerization and contain linear poly-(butyl methacrylate), $M_w = 2.2 \times 10^5$, $M_w/M_n = 2.5$. The particle surface contains a small amount of sulfate groups (1 sulfate per ca. 700 Å²). These have their origin in the use of potassium persulfate as the polymerization initiator and are attached to the ends of various PBMA chains. Films were prepared by placing a few drops of the dispersion (37 wt % solids) onto ca. 1 cm square plates of freshly cleaved mica. The films were dried slowly over 4 h at 36 °C and annealed for various periods of time in a convection oven at 70 ± 0.2 °C.

The atomic force microscope used is a commercial instrument (Nanoscope II, Digital Instruments) operated in a constant force mode. All the measurements reported here were performed under ambient conditions, using a 100-μm silicon nitride tip.

Results and Discussion

Figure 1 displays top views of a PBMA film. The uppermost image is of the nascent film, prepared at 36 °C, well above minimum film-forming temperature (MFT) of this dispersion.⁹ Under these conditions no discernible polymer diffusion occurs. The middle micrograph depicts a film aged 12 h at 70 °C, while the bottom picture is that of a film aged 97 h at 70 °C. The loss of contrast in the images of the annealed samples is real, corresponding to a diminishing of the surface roughness and fading of the boundaries between adjacent particles. In the film annealed for 97 h, the surface structure has nearly disappeared. In all these images the surface shows a high degree of order, with hexagonal packing of the latex.

It is not possible for us to align the films exactly after each annealing step. Thus the three images in Figure 1

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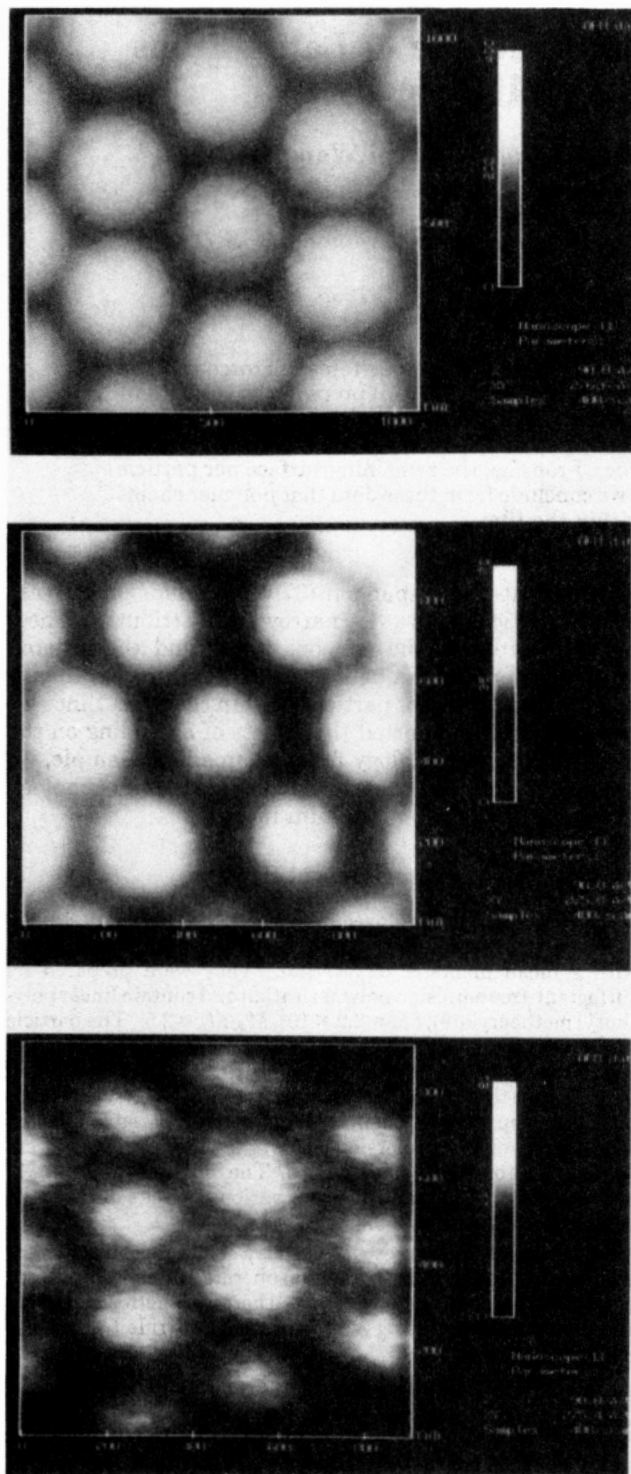


Figure 1. Atomic force micrographs (top view) of a latex film: (top) as prepared at 36 °C; (middle) after annealing 12 h at 70 °C; (bottom) after annealing 97 h at 70 °C. The gray scale range for these figures is (top) 0 to 400 nm, (middle) 0 to 70 nm, and (bottom) 0 to 21 nm.

refer to different regions of the film surface. Because of the uniformity and flatness of the film surface, it is meaningful to make comparisons between these different regions. A lower resolution image of a very similar film, prior to annealing, can be found in ref 4.

One of the advantages of AFM over other microscopies is that one can determine distance along the z -axis perpendicular to the plane of the surface. Since the film surface is highly ordered, we can define the x -axis as any line connecting the centers of adjacent particles. Plots of the film surface contour can be obtained by taking various

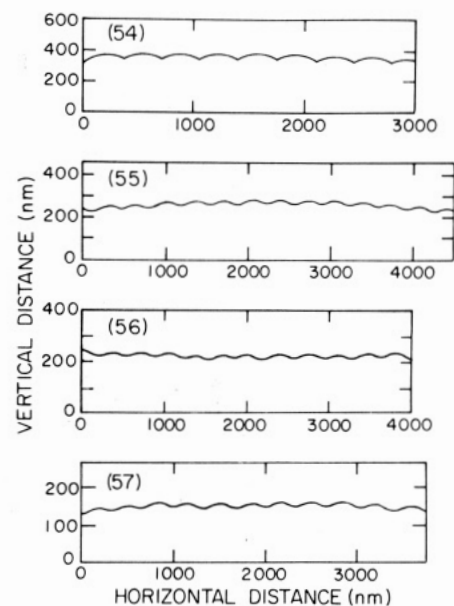


Figure 2. Tracings of the z -axis profiles of a PBMA latex film as determined by AFM: image 54, as prepared at 36 °C; image 55, after annealing 2 h at 70 °C; image 56, after 6 h at 70 °C; image 57, after 12 h at 70 °C. The reference point for the vertical scale is arbitrary. Thus the absolute values of the z -axis scale have no meaning. Values of Δz are obtained from the peak-to-valley distances in these profiles.

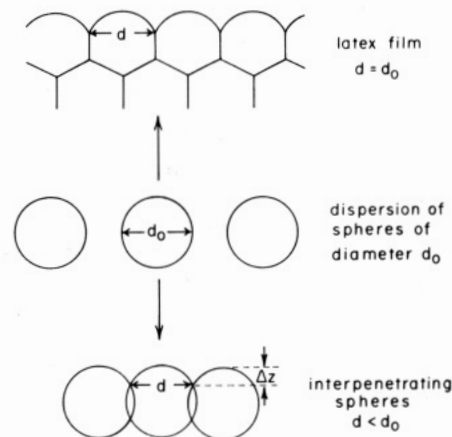


Figure 3. Drawing showing a cross section of the latex film at the surface (top), defining the interparticle spacing d , and comparing its magnitude to the latex diameter d_0 . For interpenetrating spheres (bottom), one expects to find $d < d_0$. Δz is defined as the peak-to-valley distance, as indicated, for example, for the interpenetrating spheres.

slices through the film in the x - z plane. The images generated on the computer screen were difficult to copy clearly. As a consequence we prepared traces of the film contours and display these traces in Figure 2. The top curve (image 54) represents a slice through the nascent film, and images 55, 56, and 57, respectively, are taken from the same film annealed for 2 h, 6 h, and 12 h at 70 °C.

The surface in all these images has a periodic structure where the periodicity, d , is the same as the diameter of the original latex particles, d_0 , to within experimental error. The vertical dimension, Δz , measured from peak to valley, however, is much smaller even at the earliest time we can measure. It would appear from this observation about Δz that the particles are interpenetrating even in the nascent film. However, interpenetration of particles would mean that d should be smaller than d_0 as illustrated in Figure 3, which is in contrast to our observations. We are led to

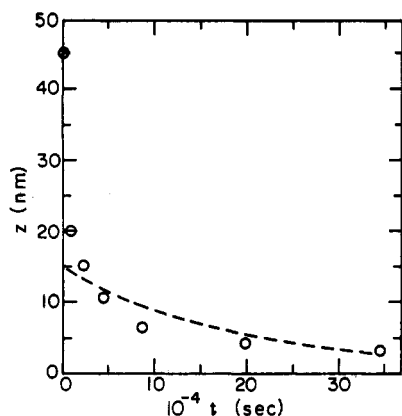


Figure 4. Plot of z vs annealing time at 70 °C for a PBMA latex film.

conclude, therefore, that in the initial stage of film formation, the particles do not interpenetrate but rather are deformed by the same osmotic and surface forces that produce rhombic dodecahedra in the bulk. However, the forces are not isotropic for the surface particles. Hence they retain their rounded shape at the side exposed to air.

The cross section of the surface (Figure 2) shows that in the nascent film, there is a sharp junction between neighboring particles, in contrast to the mild undulations present in the samples after annealing. This sharp junction corresponds to the presence of a line tension between particles in contact, which could be due to an outer film on the latex particle surface. It would appear thus that the first step in coalescence involves overcoming this line tension. We have attempted to follow its disappearance but have been unsuccessful so far, as the sharp junction disappears within the first few minutes of annealing. The contact angle, θ , may be estimated from the values of d and Δz . We reproducibly obtain a value of about 120 °C for the nascent film. This angle should be related to the nature of the latex surface, and it would thus be interesting to examine the effect of different surface groups on the latex.

One interesting aspect of the periodicity of the structures at the surface is that they are preserved throughout annealing, i.e., d remains constant with time. The peak-to-valley distance, Δz , on the other hand, decreases upon annealing. Figure 4 shows the dependence of Δz on the length of annealing time: there is a very fast drop in Δz at early times, and a slow leveling off. Since the film is being formed by the coalescence of individual particles, we can assume that the minimum energy configuration is that of a flat film and consider the particles as deformations on that film. This is not an unreasonable picture in the regime where the line tension has disappeared (i.e., after annealing); the particles appear similar to waves forced on the surface. A simple picture would indicate that such deformations should decay exponentially with time,¹⁰ with a characteristic decay time that is related to the viscosity of the medium. The line in Figure 4 corresponds to the best exponential fit to the data, excluding the point at $t = 0$. (The point at $t = 0$ does not really belong to the same data set, as it refers to the nascent film at room temperature.) It is clear that the rate of disappearance of surface corrugations is much faster than an exponential decay.

The presence of these deformations corresponds to an excess surface energy, proportional to the extra surface

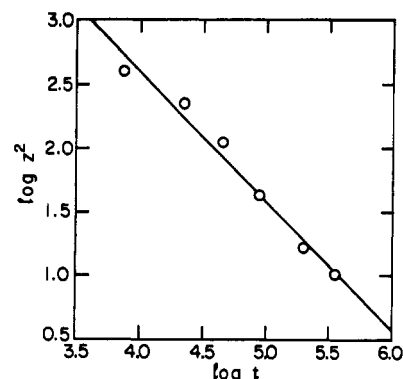


Figure 5. Plot of $\log z^2$ vs $\log t$ for the same data shown in Figure 4.

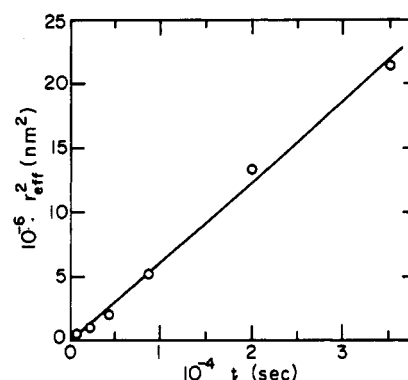


Figure 6. Plot of r_{eff}^2 vs annealing time for the PBMA latex film.

area created. The total film area can be approximated as a sum of the area of individual particles. The surface area A associated with each particle is given by the expression

$$A = \pi(R^2 + \Delta z^2) \quad (1)$$

where R is $(1/2)d$ (about 170 nm in these experiments). With extensive annealing $\Delta z \rightarrow 0$, the particle is flattened and the surface area reduces to πR^2 . $(\Delta z)^2$ is thus a measure of the extra surface area due to particle curvature. (Note that there will be a slight discrepancy between this measure of area and that of the actual smooth film, corresponding to the spaces between particles, which are expected to fill up in the annealing process.) In Figure 5 we show a plot of $\log(\Delta z)^2$ vs $\log t$. The fit to a power law is quite good, with an exponent of -1 , showing that the surface area decreases linearly with time. We do not yet have an understanding of this power law behavior.

Since it is clear that the changes in the surface structure are related to flow of the latex polymer, we would like to utilize our measurements to gain an estimate of the time scale for polymer motion that occurs at the film surface during annealing. A naive picture we can employ is to concentrate on an individual particle and to consider the decrease in Δz as a manifestation of an effective increase in latex particle size due to diffusion. While this would seem to lead to a decrease in density of the film, there will be compensation due to diffusion of material from neighboring particles. Geometric considerations give the effective particle radius, r_{eff} , as

$$r_{\text{eff}} = (1/2)(R^2/\Delta z + \Delta z) \quad (2)$$

For Brownian diffusion, this effective radius will increase with time as $(6Dt)^{1/2}$, where D is the diffusion constant of the individual polymer. Figure 6 shows a plot of r_{eff}^2 vs time and the corresponding linear fit. The fit is quite

(10) A simple model for these waves would be that of an overdamped oscillator, and the amplitude would decay exponentially with time. See for example Symon, K. R. *Mechanics*; Addison-Wesley: Reading, MA, 1971; Chapter 2.

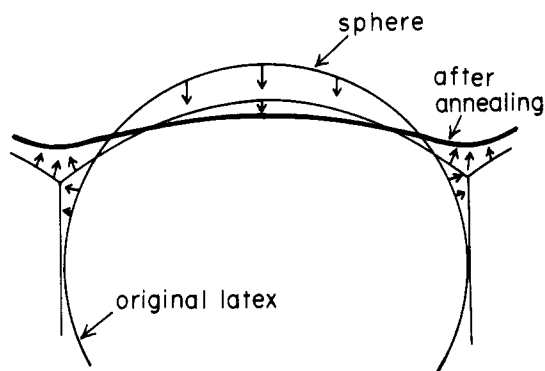


Figure 7. Drawing showing an expanded view in cross section of the evolution of shape of a latex particle at the film surface induced by annealing at temperatures well above the glass transition temperature of the polymer. The arrows indicate the directions of flow necessary to accommodate the flattening of the surface.

good, and the slope of the fitted line gives a value for D of $1 \times 10^{-13} \text{ cm}^2/\text{s}$. This is much faster (by about 4 orders of magnitude) than the diffusion constant we obtained for the same system in the bulk obtained from energy transfer measurements.^{9,11} While at least some of the discrepancy is probably due to the simple picture used in this analysis, it is not unreasonable that the diffusion near the surface

could be much faster than that in bulk due to less hindrance to motion, as well as an extra driving force from the surface energy.

We summarize in Figure 7 the picture that emerges of the formation and evolution of surface structure in these PBMA films. Before the film is completely dry, the particles order and come into contact. Deformation accompanies drying. The direction of mass flow is indicated by the downward pointing arrows at the top of the figure and the nearly horizontal arrows on both sides. Deformation leads to a structure exhibiting, in the nascent dry film, a contact angle of 120° between adjacent particles. Upon annealing at elevated temperatures, there is a rearrangement of the surface structure at the particle-particle boundary and the line tension disappears. Further mass diffusion follows, as shown by the smaller vertical arrows in Figure 7, and leads to a decrease in Δz and smooth oscillations in the film surface. Fitting the data to a simple diffusion model leads to the suggestion that surface polymer chains undergo diffusion with a characteristic diffusion coefficient 10^4 larger than that for the polymers in the interior of the film.

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