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Surface molecular diffusion in latex films observed by atomic force microscopy

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Abstract

Surface molecular diffusion in a latex film has been investigated by atomic force microscopy. Deformation of the particles in the plane of the film of a real latex system did not change the centre-to-centre spacing, but the peak-to-valley distance y decreased upon annealing. The theoretical and also the experimental relationship between y and time t is given by the equation $y(t) = y(0)\exp(-t/\tau)$ where τ is a constant, which is related to surface tension, particle size and the surface molecular diffusion coefficient. By measuring the change of y with time, the surface molecular diffusion coefficient may be obtained. The surface molecular diffusion coefficient for a poly(methyl methacrylate-*co*-butyl acrylate) (50:50) copolymer latex film at 65°C was found to be 0.9×10^{-13} cm^2/s. Surface molecular diffusion in the latex film is driven by the surface tension or surface free energy. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Over recent years, concern for the environment has generated many instances where there is a need to turn from a polluting technology to one that is more benign. Since these changes are driven by non-technological factors, this can have the result that the new system has poorer performance characteristics than the technology being replaced. Under such circumstances, it becomes important to understand the origins of good performance, so that adequate or even improved performance can be achieved with a new technology that is safer to the environment.

One current example of this situation is the impact on coatings technology of stricter regulation of volatile organic compound emissions. Because of these restrictions, the use of waterborne latex-based coatings is expanding into areas such as automotive and industrial markets, which have resisted this change because the waterborne latex coatings are as yet often unable to achieve the same high level of performance as the traditional solvent-based systems [1].

In solvent-based coatings, the polymer molecules are entangled and fully interpenetrating as they are applied to the surface. Solvent evaporation leaves a uniform film of low permeability. In latex coatings, the polymers are packaged in discrete particles, which must coalesce during drying and subsequent ageing to form a protective film. Such films are more permeable, especially to moisture, than the corresponding solvent-based films [2]. These films provide poorer protection of the underlying substrate. There are many reasons for the differences in properties between the two types of coatings, but it is clear that the "quality of coalescence" of latex coatings has an important effect on final film properties [3]. This process of coalescence is one of the most important aspects of latex film formation. An understanding of the mechanism by which coalescence occurs is crucial for further advances in this area.

Traditionally, the film formation process has been considered in terms of three sequential steps: water evaporation to the point where the particles begin to touch (stage 1), deformation of the latex spheres to space-filling polyhedra induced by surface and osmotic forces associated with passage of water from the interstitial spaces (stage 2), and coalescence of the deformed particles to form a mechanically continuous film (stage 3) [4,5].

Many studies of the individual stages, utilising a variety of different techniques, have been published. For example, Baas-Bar Ilan and co-workers [6] have used transmission electron microscopy (TEM) to investigate concentrated aqueous polystyrene latex dispersions typifying stage 1.

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Atomic force microscopy (AFM) [7,8] has been utilised recently to observe the surface topography and packing of a poly(butyl methacrylate) (PBMA) system in the stage 3 state. The molecular interdiffusion phenomena of stage 3 have also been extensively studied by such techniques as non-radiative energy transfer methods [9] and small-angle neutron scattering [10]. The time dependence of particle deformation occuring at the surface of a PBMA latex during stage 3 has been measured by means of AFM by Goh et al. [11]. They calculated the surface molecular diffusion coefficient based on the classical diffusion model and found it to be 1×10^{-13} cm^2/s, which is three or four orders of magnitude larger than that obtained by using a fluorescence technique [12] (10^{-16}–10^{-17} cm^2/s). The difference was attributed to the extra driving force from the surface energy, which causes faster diffusion near the surface than in the bulk [11].

In this paper, we will study surface molecular diffusion during latex film formation both experimentally by means of AFM and theoretically in the stage 3 situation. It is perhaps appropriate here to point out that a semantic confusion exists in the literature on latex film formation, in that the

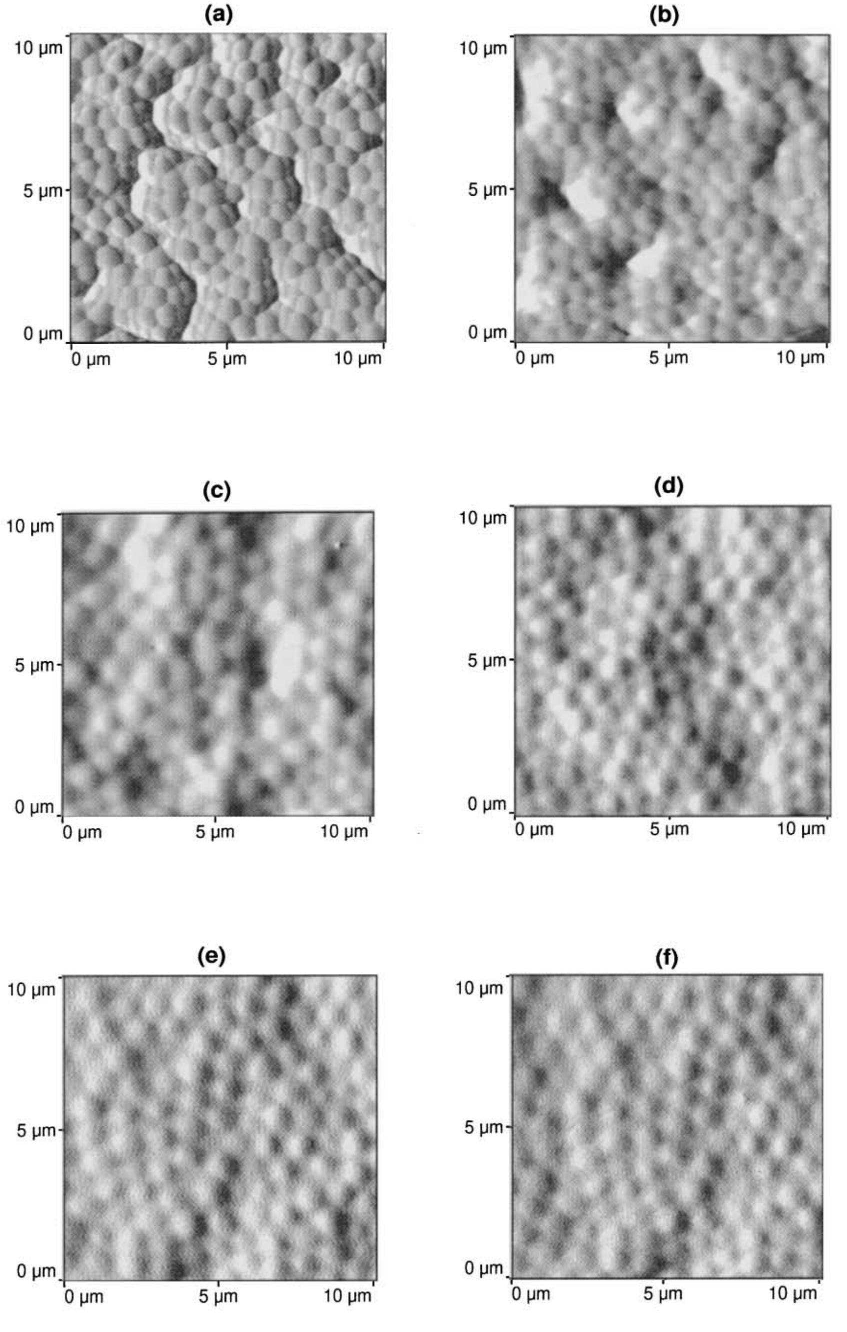

Fig. 1. 10 µm × 10 µm AFM images of the morphology of the poly(methyl methacrylate-*co*-butylacrylate) copolymer latex film versus annealing time at 65°C: (a) 0, (b) 1, (c) 5, (d) 40, (e) 100 and (f) 140 h.

terms "coalescence" and "film formation" are often used as synonyms. The two terms are not synonymous. Coalescence implies the fusion of latex particles by polymer interdiffusion across the particle boundaries, while film formation only implies that a film is formed by the distortion of the particles to eliminate the interstitial voids. Here, we regard stage 3 as coalescence.

2. Experimental

Poly(methyl methacrylate-*co*-butyl acrylate) (50:50, wt/wt) lattices were prepared according to the following method. Ammonium persulphate (AP), sodium dodecylbenzenesulphonate (SDBS), methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BA) were obtained from Aldrich. Azoisobutyronitrile (AIBN) was supplied by BDH. All the monomers were purified by passing through a column packed with inhibitor remover. The polymerisations were performed under a flowing nitrogen atmosphere in a 600-ml reaction vessel equipped with stirring. The reaction vessel was kept in a water bath maintained at 85°C. Deionised water (200 ml) containing 0.3 g SDBS were added and the vessel purged with nitrogen for 20 min. Then 0.25 g AP and 20 ml 1:1 MMA/*n*-BA were added and allowed to react for 15 min. The temperature of the water bath was then reduced to 80°C. MMA/*n*-BA (1:1, 80 ml) and 0.15 g AP dissolved in 30 ml water were simultaneously fed into the reaction vessel via two peristaltic pumps over a period of 3 h. After the monomer addition was complete, the latex was allowed to post-react for a period of 1 h to ensure the completion of polymerisation. Films were prepared by placing a few drops of the latex (about 35% solids content) onto ca. 1 cm^2 plates of freshly cleaned glass. The film was dried slowly over 24 h at 25°C and annealed for various periods of time on a hot stage at 65 ± 0.5°C. The glass transition temperature of the film was 17°C.

Instrumentation: AFM experiments were performed in the contact mode using a TopoMetrix 1000 Explorer [13] fitted with a silicon nitride probe on a V-shaped cantilever.

3. Results and discussion

Fig. 1 displays a series of AFM images, which show the changes of morphology of the poly(methyl methacrylate-*co*-butyl acrylate) latex film with annealing time at 65°C. Fig. 1(a) is of the film as prepared at 25°C. The effect of subsequent annealing on the surface morphology can be clearly seen. The loss of contrast in the image of annealed samples is real, corresponding to a diminishing of the surface roughness and a fading of the boundaries between adjacent particles.

With a Topometrix 1000 AFM, it is possible to examine the film in exactly the same location after each annealing step. Therefore, it is important to stress that these images shown in Fig. 1 refer to the same region of the film surface.

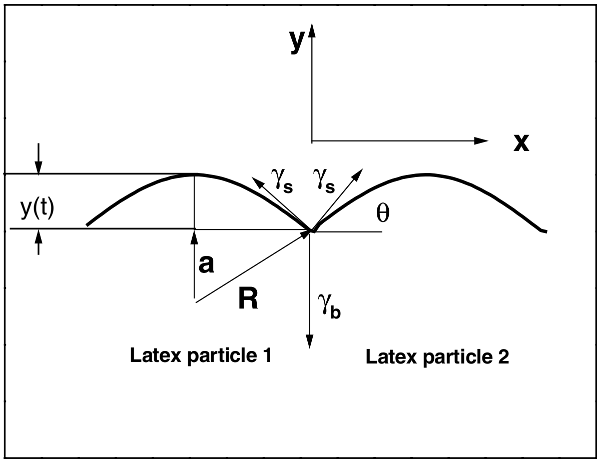

Fig. 2. Schematic of the theoretical analysis for the surface molecular diffusion in latex films.

Goh et al. [11] showed 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. Our results also show that the deformation of the particles in the plane of the film does not change the centre-to-centre spacing.

In early stages of annealing, there is a sharp junction between neighbouring particles and in the late stages, the sharp junction becomes flattened. This may result from surface molecular diffusion. Although the film was annealed for 140 h, the surface structure did not disappear. In all these images, the surface showed a high degree of particle ordering.

The distance, $y(t)$ (see Fig. 2), along the y-axis perpendicular to the plane of the surface [11] was determined. The vertical dimension measured from particle peak-to-valley is what decreases upon annealing [11]. Fig. 3 shows the average dependence of $y(t)$ on annealing time. This average was obtained from measurements conducted on between 40 and

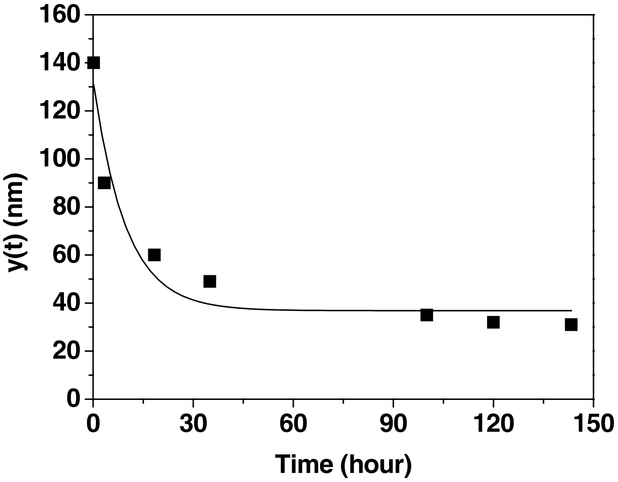

Fig. 3. Dependence of y for the poly(methyl methacrylate-*co*-butyl acrylate) copolymer latex film on annealing time at 65°C.

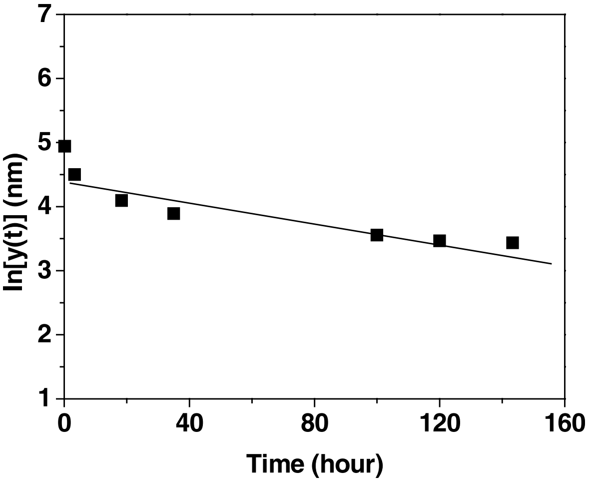

Fig. 4. Dependence of $y(t)$ for the poly(methyl methacrylate-*co*-butyl acrylate) copolymer latex film on annealing time at 65°C on a logarithmic scale.

50 pairs of particles. The dashed line in Fig. 3 corresponds to the best exponential fit to the data. Fig. 4 is the plot of $\ln[y(t)]$ vs. t (we omitted the value at $t = 0$ because the point at $t = 0$ does not belong to the same data set as it refers to the film at room temperature [11]). The plot clearly shows that $\ln[y(t)]$ vs. t is approximately linear, i.e. $y(t) = y(0)\exp(-t/\tau)$. Since the film is being formed by the coalescence of individual particles, it can be assumed that minimum surface free energy is that of a flat film. Goh et al. [11] obtained the same results, which decay exponentially with time. Goh suggested that the particles appear as being similar to waves forced on the surface and a simple picture would indicate that such deformation should decay exponentially with time, with a characteristic decay time that is related to the viscosity of the medium. It is possible that surface molecular diffusion occurs. Later a theoretical analysis will tend to prove this point.

For the case of surface structure development during latex film coalescence, consider the following points.

1. Molecular diffusion in the surface of the latex film is driven by the surface tension or surface free energy of the latex particles.
2. Surface tension-driven processes will yield values of the surface molecular diffusion coefficient D_s.
3. A section normal to the boundary between particles and the surface is shown is Fig. 2. This local equilibrium at the intersection is attained when

   $$\theta = \arcsin(\gamma b/2\gamma_s) \tag{1}$$

   where θ is defined in Fig. 2. γ_s is the surface tension of the two solid–air surfaces and γ_b is the surface tension of the particle–particle boundary (see Fig. 2).
4. Deformation of the particles in the plane of the film formed from a real latex system does not show any change in the centre-to-centre spacing, but the peak-to-valley distance y decreases upon annealing (see Fig. 2).

The surface becomes flat with time. The macromolecules in a surface with a radius of curvature r have a higher chemical potential than the macromolecules in a flat surface at the same pressure and temperature. The difference in chemical potential $\Delta\mu$ is given by the Gibbs–Thomson equation [14,15]:

$$\Delta\mu = -\gamma\Omega/r = -\gamma\Omega C \tag{2}$$

where Ω is the volume per molecule and C the curvature of the surface. The precise relationship [14,15] for C is as follows:

$$C = \mathrm{d}^2y/\mathrm{d}x^2/[1 - (\mathrm{d}y/\mathrm{d}x)^2]^{3/2} \tag{3}$$

Assuming $(\mathrm{d}y/\mathrm{d}x)^2$ is much less than 1, $\Delta\mu$ can be approximated by the following equation:

$$\Delta\mu = -\gamma\Omega\,\mathrm{d}^2y/\mathrm{d}x^2 \tag{4}$$

Consider that the flux experienced in the surface in the x-direction is given by the average surface diffusion coefficient D_s, the average density of segments ρ and the average force per segment $-\partial\mu/\partial x$. Thus, according to Fick's law of diffusion [3], the general flux J is given by:

$$J = -D_s\rho/(\mathrm{k}T)\,\partial\mu/\partial x \tag{5}$$

where k is the Boltzmann constant and T the temperature.

If we consider an element of surface area dx wide and having unit length, the flux of material in this element is proportional to

$$\mathrm{d}J = J_s - J_{s+\mathrm{d}s} = -\partial J/\partial x\,\mathrm{d}s = D_s/(\mathrm{k}T)\,\partial^2\mu/\partial x^2 \tag{6}$$

This flux decreases the surface, so $\mathrm{d}J/\mathrm{d}x$ is proportional to the rate of decrease of the surface, $(\partial y/\partial t)$. To obtain an equality instead of a proportionality, it is necessary to assume an effective depth for the high-diffusivity surface layer as is done in the case of grain boundary diffusion. If this depth is defined as a radius of gyration of a segment r_g, the number of molecules per second entering the element of surface area is $\mathrm{d}Jr_g$ and the rate of decrease of the surface element is the volume accumulated per second over the area [14,15] or

$$\mathrm{d}Jr_g 1/\mathrm{d}x = \partial y/\partial t = D_s r_g/(\mathrm{k}T)\partial^2\mu/\partial x^2 \tag{7}$$

Using Eq. (4) leads to the following diffusion equation:

$$\partial y/\partial t + \Omega\gamma_s D_s r_g/(\mathrm{k}T)\,\partial^4 y/\partial x^4 = 0 \tag{8}$$

The general solution of Eq. (8) is

$$y(x,t) = A_0\exp(-\lambda D_s r_g\Omega\gamma_s t/(\mathrm{k}T))\sin(\lambda^{1/4}x) \tag{9}$$

$$\lambda = \pi^4/[16((R^2 - a^2)^2)] \tag{10}$$

For experiments involving latex film formation, we choose a fixed x_c value, say

$$x = x_c = (R^2 - a^2)^{1/2} \tag{11}$$

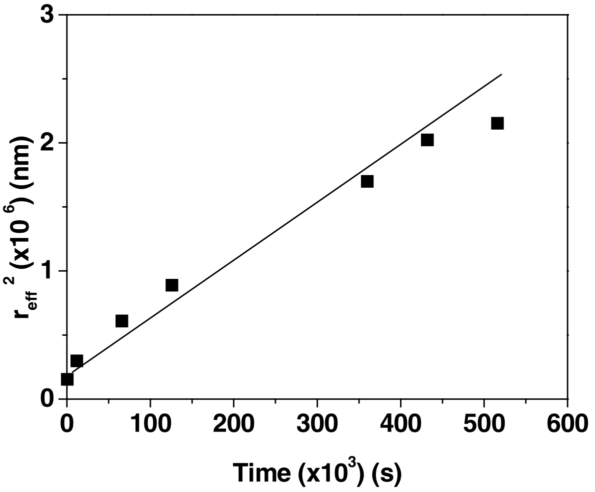

Fig. 5. r_{eff}^2 vs. annealing time.

At this point, we have

$$y(t) = y_0 \exp(-\lambda D_s r_g \Omega \gamma_s t/(\mathrm{k}T)) = y_0 \exp(-t/\tau) \tag{12}$$

where y_0 is the value of $y(x,t)$ at $x = x_c$ when $t = 0$. Obviously, the predication of the model is in good agreement with our experimental results (see Figs. 3 and 4) and also with Goh et al. data [11]:

Choosing Ω to be equal to $4\pi r_g^3/3$, yields the following equation:

$$y(t) = y_0 \exp(-(3/4)^{1/3}\pi^{11/3}/[16(R^2 - a^2)^2]D_s\Omega^{4/3}\gamma_s t/(\mathrm{k}T)) \tag{13}$$

Measuring the change of $y(t)$ with time, the characteristic time τ in Eq. (12) can be obtained. According to Eq. (13), the surface diffusion coefficient D_s may be obtained.

Consider that $\Omega \approx 10^{-20}$ cm^3, $k = 1.38 \times 10^{-23}$ J/°C, and $\gamma_s \approx 30 \times 10^{-7}$ J/cm^2 [16]. Fitting the experimental data, D_s value for the poly(methyl methacrylate-*co*-butyl acrylate) copolymer latex film at 65°C was found to be about 0.9×10^{-13} cm^2/s.

The surface diffusion can also be discussed based on Brownian diffusion [11]. The relationship between effective radius r_{eff}, $y(t)$ and t is as follows [11]:

$$r_{\mathrm{eff}} = 0.5[R^2/y(t) + y(t)] \tag{14}$$

$$r_{\mathrm{eff}}^2 = 6Dt \tag{15}$$

where D is the diffusion coefficient. From the plot of r_{eff}^2 vs. time, D can be obtained. Fig. 5 is the plot of r_{eff}^2 vs. time. The slope of the fitted line gives the value of D about 1.1×10^{-13} cm^2/s. The value is similar to that obtained by Eqs. (12) and (13).

4. Conclusions

AFM can be used to observe surface molecular diffusion of latex films. The peak-to-valley distance y decreases with annealing time. The theoretical relationship between y and time t can be expressed as follows:

$$y(t) = y_0 \exp(-(3/4)^{1/3}\pi^{11/3}/[16(R^2 - a^2)^2]D_s\Omega^{4/3}\gamma_s t/(\mathrm{k}T))$$

By measuring the change of $y(t)$ with time, the dynamics of surface molecular diffusion can be studied and the surface molecular diffusion coefficient obtained. The surface molecular diffusion coefficient of the poly(methyl methacrylate-*co*-butyl acrylate) copolymer latex film at 65°C was found to be 0.9×10^{-13} cm^2/s.

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