Chapter 6

6 Surfactant Distribution in Latex Films

6.1 Introduction

Colloidal polymer particles are made by techniques of emulsion polymerisation, as described in Chapter 1. To emulsify the monomer phase in conventional emulsion polymerisation, and to create micelles that serve as seed particles, one or more surfactants are used. Surfactants are amphiphilic molecules that have a hydrophilic head group and a hydrophobic tail, causing them to adsorb at interfaces and to self-assemble. They impart colloidal stability (through steric or charge effects) and encourage monodispersity of particle size. Although it is possible to perform surfactant-free emulsion polymerisation (Goodwin 1971), which avoids the complications of surfactant migration and segregation, it is difficult to obtain high volume fraction latices with this method. Hence, industrial latices typically contain a large amount of surfactant (on the order of 2 wt. % of the polymer). Surfactants are usually classified as either non-ionic, cationic or anionic, depending on the charge on the hydrophilic head of the molecule.

An often desired scenario is for uniform distribution of surfactant through a film, although this is rarely observed in practice. This chapter examines how and why surfactants are distributed non-uniformly in latex films. Previous studies into surfactant stratification are summarised, as well as the experimental techniques commonly used to observe the distribution. A model is presented for predicting the distribution of surfactant, by following the convective and diffusive mass transport. This allows the distributions to be controlled through the adsorption isotherm of surfactant on the particle surfaces.

There is a large and extensive literature relating to surfactant distributions in latex films. The earliest work dates back to 1936 (Wagner and Fischer 1936) and an overview of twentieth century research is provided by Hellgren et al. (1999). As will be discussed in this chapter, surfactants are implicated in diminishing film properties and performance, and are suspected of influencing the film formation process itself. This chapter aims to correlate and explain the vast array of experimental observations.
An example of non-uniform surfactant distribution in an adhesive film is shown in Fig. 6.1. Despite being film formed at 60°C (over 100°C above the glass transition temperature of −45°C), the latex particles are not coalesced but remain as discrete entities. Upon rinsing the film with water, however, the particle boundaries become blurred, as shown in Fig. 6.1b, as polymer interdiffusion starts to take place. The conclusion (supported by chemical analysis) is that a water-soluble component – consisting of surfactants, polymers and oligomers in the latex serum phase – is partitioning between the particles and preventing them from coalescing. This is an instance where the surfactant distribution affects the final morphology at a film surface.

Fig. 6.1 Phase contrast AFM images of an acrylic latex (based on a EHA-BMA-MMA copolymer) film-formed at 60°C for three minutes. The copolymer $T_g$ is about −45°C. a An image of the film as-dried, showing the particles hindered in their deformation and coalescence. b An image of the same film is shown after rinsing with water. The particle boundaries are less distinct as a result of particle coalescence. (Images courtesy of J. Mallégol)

### 6.1.1 Where Can Surfactant Go in a Dried Film?

A useful starting point is to consider the possible fate of a surfactant in a dried film. Fig. 6.2 shows schematically five possibilities for the final location of surfactant. For instance, when various types of surfactant (anionic, cationic and ionic) are added to a latex dispersion, the surfactant might be enriched at the air interface, at the substrate interface, or at both (Zhao et al. 1987, Belaroui et al. 2003). These two positions are shown as (i) and (ii), respectively, on the diagram. Strongly absorbed surfactants will remain on the particle surfaces during film formation and thereby be trapped along particle boundaries (iii). Trapped surfactant is suspected of creating hydrophilic pathways in a film. Indeed, in nominally dry latex films, water has been found to be bound to the ionic headgroups of