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On some aspects of latex drying – ESEM observations

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ABSTRACT

Environmental scanning electron microscopy has been employed to study the drying behaviour of a non-film forming polymethyl methacrylate (PMMA) based latex system. The approach adopted for this study differs slightly when compared to those used previously. Here, by allowing the latex to initially film form, it has been possible to make observations and conclusions regarding the structural development of the specimens under investigation not only in 2D, but also in 3D. The results clearly demonstrate that upon drying, particle packing can yield hexagonal close packed (HCP), square close packed (SCP) and random arrangements, including voids and surface defects that result in the formation of a crystal-like structure. Based on the experimental observations some modifications to the latter stages of the film formation mechanism taking place at temperatures (T) lower than the system glass transition temperature (T_g) have been proposed.

1. Introduction

Polymer lattices, with their wide range of applications, have been the subject of many theoretical and experimental studies. Latex can be defined as a mixture of usually spherical particles (whose size is larger than that of a molecule, but small enough not to be seen by the naked eye), dispersed throughout a liquid. When used for its traditional applications, for example as paint or adhesive, the latex is applied in its wet state to a surface and allowed to dry. This process, commonly referred to as film formation, is associated with the evaporation of water and is generally agreed to consist of four main stages [1–9]: Stage 1 – dilute dispersion of polymer particles in solution; Stage 2 – a more concentrated particle suspension with water filled interstices; Stage 3 – if the temperature (T) is greater than the minimum film formation temperature (T_{mff} or MFFT) a more ordered array of deformed particles can form, and finally; Stage 4 – if $T > T_g$ (glass transition temperature), formation of a homogeneous, molecularly continuous film, a direct result of inter-diffusion of polymer chains across particle boundaries. These four stages are illustrated in Fig. 1.

A number of detailed studies have subsequently been performed that have provided further insight into the drying behaviour of different colloidal compositions. Keddie et al. [10] used environmental scanning electron microscopy and multiple-angle-of-incidence ellipsometry (MAIE) in the study of latex film formation. They concluded that an intermediate stage, between II and III, has been omitted in the conventional descriptions. The stage, defined as II*, is characterized by a randomly packed array of deformed particles which still contain water-filled interstices.

More recently, Keddie and co-workers [11,12] investigated the possibility of creating heterogeneous films, by mixing carbon nanotubes (CNTs) with waterborne polymer particles. It was found that the mechanical properties of the nanocomposite coatings can be greatly improved, while maintaining their optical clarity. However, it is important to note that all of the above studies were carried out using continuous polymer films.

In 2008, Dragnevski et al. [13] used environmental scanning electron microscopy (ESEM) to study the film formation mechanisms of two acrylic latex compositions, defined as standard (carboxymethyl cellulose stabilised) and novel (stabilised with a polysaccharide derived from agricultural waste). The ESEM analysis revealed that the microstructure of the standard system consisted of individual particles and upon evaporation a continuous film was formed, which is consistent with the current models. However, in the case of the novel system, the microstructure consisted of individual particles and clusters and during evaporation a discontinuous film was formed with voids present within its structure. Based on the experimental evidence, the authors proposed a modification to the film formation mechanism for the novel latex system.Although it is thought that the schematic diagram shown in Fig. 1 gives a good overview of the film formation process, when drying in air, it is by no means complete. The transition between Stage 1 and Stage 2 involves several mechanisms in order to achieve a close-packed latex system. These were reflected in a recent study by Routh et al. [14] who considered the vertical particle distribution in drying polymer lattices. It was shown that due to the high water concentration gradient created by the boundary between the colloid and the air surrounding it, water loss by evaporation

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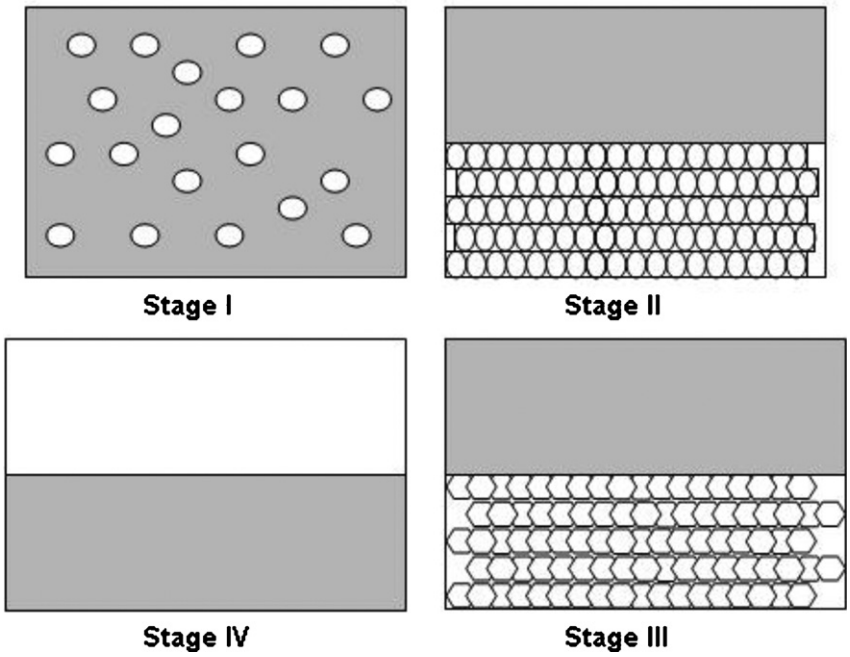

Fig. 1. Schematic diagram of the four stages of latex film formation.

is greatest at the film surface. Therefore it can be suggested that this would lead to localised drying at the surface inducing an upper close packed region on the top where the particle volume fraction is greatest. Thus the high water concentration gradient would continue downwards until all the water has been removed. Below the region of close packing, it has been suggested that Brownian motion of the particles occurs and the presence of water encourages the diffusion of the polymer into the water solvent [15]. Hence, the degree of diffusion would largely determine the continuity of volume fraction in dried lattices. A good indicator of particle continuity is given by the Peclet number, which represents the particle rate of convection divided by the diffusion rate. It is defined as:

$$Pe = \frac{6\pi\mu R_0 H\dot{E}}{kT}$$

where, μ = solvent viscosity, R_0 = particle radius, H = film thickness, $\dot{E}$ = evaporation rate and kT the thermal energy. Consequently, when $Pe \ll 1$, the degree of diffusion is strong and one can expect a uniform particle distribution. When $Pe \gg 1$, large discontinuities may arise in the film.

It has also been shown that inter particle electrostatic forces of attraction and repulsion also affects how the film forms [16]. These forces influence how individual and groups of particles stick together. Brown [1] claimed that coalescence of particles occurs when forces favourable for film formation, such as van der Waals forces and capillary forces, outweigh repulsive forces such as electrostatic repulsion. Denkov et al. [17] identified capillary forces due to inter particle menisci as the main driving force for particle ordering and the way particles transport towards areas of high volume fraction.

In addition to vertical particle distributions, similar horizontal drying mechanisms affect the formation of latex films [18]. Due to the presence of a surface and a meniscus at the edges of colloidal dispersions, it is often observed that drying initiates here. The surface at the edge allows for water removal and therefore a locally higher volume fraction is created, just like the mechanism discussed in vertical drying. The thinning of film due to the meniscus encourages particle packing and mass transfer towards the film edge caused by the pressure gradient from the capillary forces. This horizontal drying mechanism creates three main regions, moving from the film edge towards its centre: dry particles at the film edge, then a region of higher particle volume fraction with the initiation of particle close-packing, and finally the dilute colloidal dispersion furthest from the edge. The arrangement creates a drying front that travels away from the colloid edge until the whole of the material has dried [20]. Fig. 2 illustrates the different regions in the horizontal drying mechanism.

Once the evaporation of water at constant rate has completed and resulted in the formation of an ordered structure, as suggested above, certain conditions drive the progress of film formation. If the drying temperature does not surpass the minimum film formation temperature, then the resulting material will dry with undeformed particles in close contact with each other creating a porous system with interstitial gaps (through which water can pass). If the temperature does exceed the MFFT, capillary forces and surface tension will cause the particles to deform. At temperatures well above the MFFT and above the polymer glass transition temperature, complete deformation of the particles takes place and particle inter-diffusion of polymer chains occurs to create a non-porous homogeneous film [19].

As mentioned above, when used for its traditional applications, i.e. as paint or adhesive, this electrically insulating material is applied in its wet state and allowed to dry under ambient conditions. Therefore, conventional electron microscopy, with its extreme drying and sample preparation requirements, is not suitable for the examination of lattices in their natural state. On the

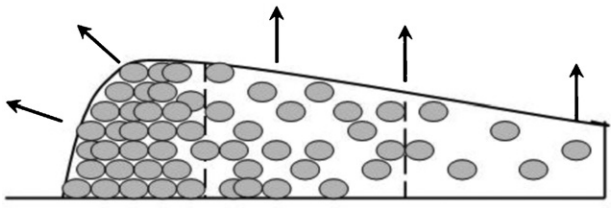

Fig. 2. Schematic representation of how particle concentration influences film thickness.