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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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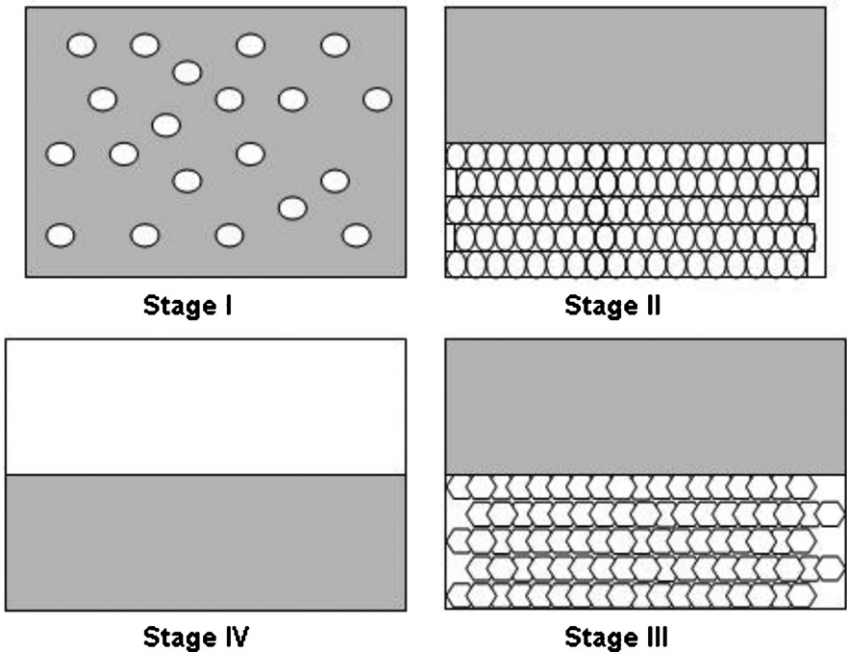

Fig. 1. Schematic diagram of the four stages of latex film formation.

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

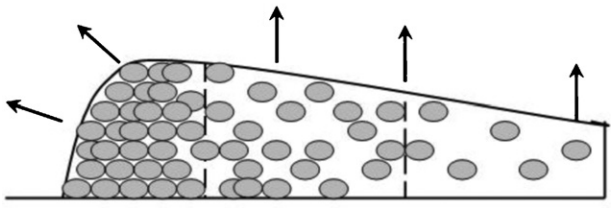

Fig. 2. Schematic representation of how particle concentration influences film thickness.

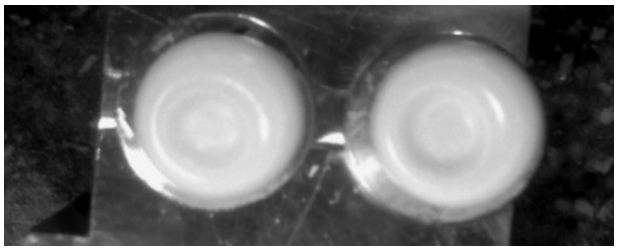

Fig. 3. Photograph of the dried latex disks cast onto aluminium SEM stubs.

other hand, environmental scanning electron microscopy (ESEM), also referred to as "wet" or "leaky" scanning electron microscopy [20], offers the possibility of imaging insulating materials in their hydrated state, without the need of conductive coatings. Unlike conventional electron microscopy, where high vacuum is maintained throughout the instruments, ESEM is based on the use of a multiple aperture graduated vacuum system, which allows specimens to be imaged under water vapour or other auxiliary gases, such as nitrogen or nitrous oxide [21]. In this way, the chamber can be held at pressures between ~133 Pa and 1330 Pa [22], while the gun and column remain at pressures of $\sim 10^{-4}$ Pa. Moreover, by using a correct pumpdown procedure [23] and by controlling the temperature of the specimen, which in the ESEM is usually done by using a Peltier stage, dehydration of wet samples can be inhibited and hence samples can be imaged in their "natural state". Furthermore, by taking into consideration the saturated vapour pressure (SVP) curve for water as a function of temperature [23] and by increasing the temperature of the specimen or reducing the chamber pressure, it is possible to produce evaporation conditions within the specimen chamber, which allows examination of the dynamic processes, such as of film formation. From the above, it is also clear that in the case of ESEM, the electrons emitted from the specimen, whether they are secondary or higher energy backscattered electrons, have to travel to the detector through the gas-containing chamber and hence will undergo collisions with gas molecules, which can be either inelastic or elastic. In this way a cascade amplification process occurs, so that many more electrons are detected than were originally emitted from the sample [15]. A highly desirable effect of the cascade amplification process is that positive ions are formed which drift back to the surface of the specimen, where they tend to neutralise the usual build up of charge associated with electron microscopy of insulators. Thus in ESEM, insulating materials can be viewed without the need of conducting coating and hence in their natural state.

In this study environmental scanning electron microscopy was employed to investigate latex specimens in the final stages of film formation with the aim of both evaluating the versatility of the experimental technique and providing further information on less investigated aspects of film formation, such as through-thickness and surface particle distribution and packing.

2. Materials and methods

The aqueous latex used in this study was supplied by the Department of Chemistry, University of Oxford and consisted of polymethyl methacrylate (PMMA) particles with diameter in the region of 700–800 nm, determined by means of light scattering apparatus. The latex was initially 75 wt.% polymer. The microstructural analysis was carried out on a Carl Zeiss Evo LS15 Variable Pressure Scanning Electron Microscope, equipped with a LaB_6 gun source and a range of detectors for electron imaging. The specimens were cast directly onto standard aluminium SEM stubs (Fig. 3). The colloid was then allowed to film form for 24–48 h at room temperature before being examined under the ESEM. Imaging was carried out under a nitrogen atmosphere (~10 Pa), at accelerating voltages in the region of 12.5–13.5 kV and working distances in the region of 10–15 mm. The combination of these imaging conditions resulted in minimal beam damage of the specimens during examination.

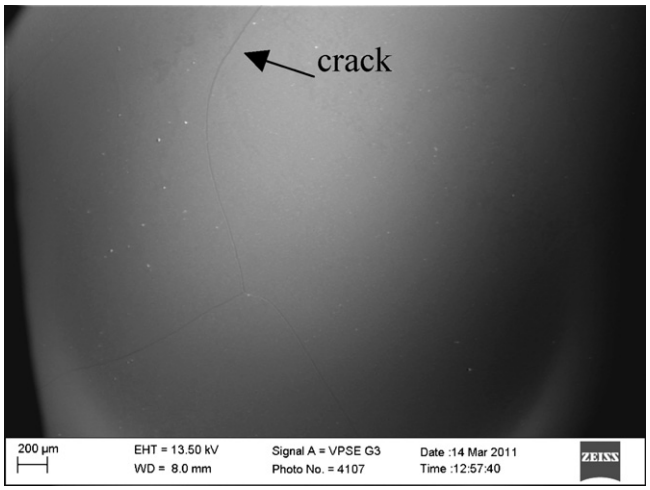

Fig. 4. Low magnification ESEM image of the surface of a dried latex specimen.

3. Results and discussion

A low magnification ESEM image of the dry latex specimen is shown in Fig. 4, from which a number of interesting features can be identified. The presence of cracks suggests that drying has not experienced temperatures above the polymer's glass transition temperature, as would be required to form a homogeneous film. Due to the concentric brightening of the image observed towards the bottom corners, it is also evident that the centre of the disk is thinner than its edge. This thickening around the edges is consistent with the horizontal drying mechanism discussed in the earlier part of this paper, and is also observed in Fig. 3. It would therefore be reasonable to assume that drying initiated around the edge of the specimen due to the presence of the meniscus and locally higher ratio of surface area to colloid volume, which encourages particle packing and water loss respectively.

Hence, the thin thickness observed at the centre of the disk is a result of the particles migrating towards the edge as the material dries. This would inevitably reduce the concentration of the particles towards the disk centre so that when the water from that region is eventually removed; fewer particles would be available to create a thicker centre. The typical variation in specimen thickness after drying is shown in Fig. 5.

Further examination of the latex specimens at higher levels of magnification, especially along crack faces, revealed features that give insight into the vertical drying mechanisms of the colloidal system (Fig. 6a and b). From the presented images, it is clear that, as already suggested, the latex has not formed a homogeneous

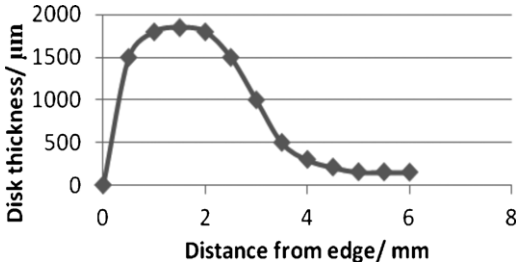

Fig. 5. Typical material thickness variation.

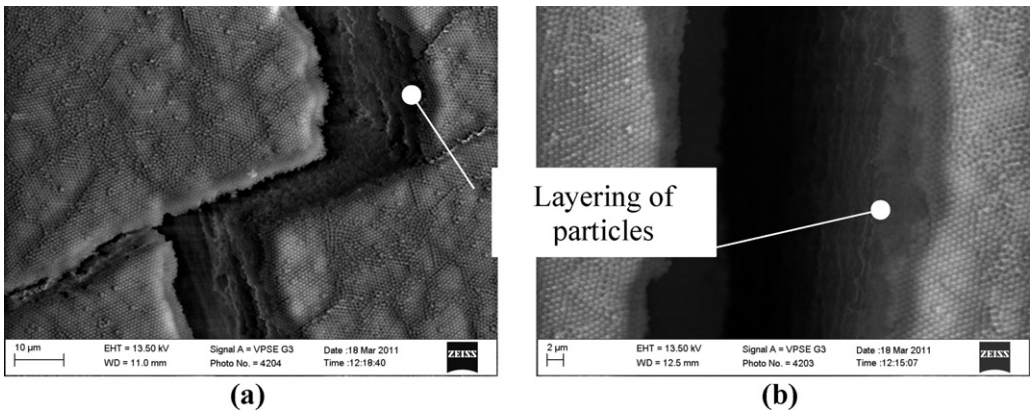

Fig. 6. Higher magnification ESEM images of cracked faces observed in film-formed latex specimens.

and continuous film. The ability to observe individual particles also reveals the porous nature of the material and verifies that particle deformation during film formation was minimal. It also demonstrates that particle inter-diffusion of polymer chains has not taken place. This results in an unstable material, as particles are held together by weak van der Waals forces (when compared to the covalent bonds present in inter-diffused systems), and many surfaces are potentially present where energy can be released. Closer inspection of the crack faces present in the images demonstrates that layers of particles arranged themselves as one would expect to achieve from a drying front that travels vertically down through the colloid system. This is in line with the model presented by Routh et al. [14].

The ESEM image in Fig. 7 is at a magnification level where surface features are identifiable, but individual particles are not. It can be seen that the latex surface is not smooth or continuous: there appear to be numerous defects. These defects could be due to the presence of air bubbles trapped in the casting process, differing drying rates in different areas of the material and the presence of surfactants used in the manufacturing process of the PMMA colloid. All of these factors will have an effect on the eventual particle arrangement observed at the surface. However, examination of the latex surface at higher magnifications, as shown in Fig. 8, allows individual polymer particles to be observed. The image reveals the existence of voids in the latex which appear to manifest themselves in regions of irregular particle packing. The irregular packing could be a result of different drying rates and/or variations in particle sizes.

Further examination of the dried specimens at lower magnifications also revealed that the latex surface had an apparently crystalline arrangement (Fig. 9). Lines on the individual "crystals" suggest that they could be an indication of the particle alignment within the "crystal". Examination of the surface at higher magnifications (Fig. 10) shows that this is in fact the case. It highlights different packing arrangements and reveals that their alignment is not uniform. Both hexagonal (HCP) and square (SCP) close packing groups are distinguishable within the structure of the latex. The areas of regular close packing are often separated by areas with irregular particle arrangements. This variation in particle packing and arrangement could be a result of the drying of a two phase latex which had surface particle groups separated by dilute colloid.

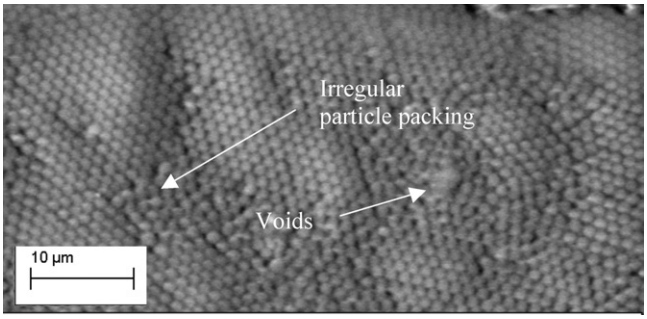

Fig. 8. ESEM image of a latex surface revealing voids and irregular packing.

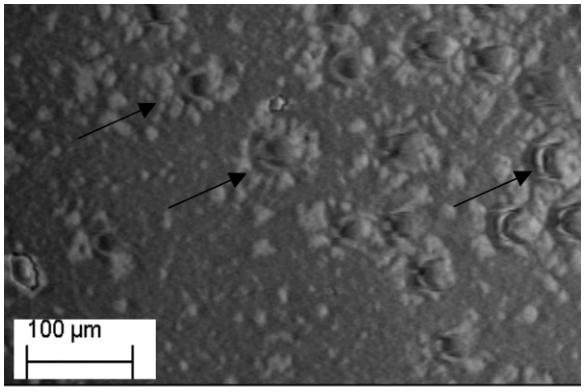

Fig. 7. Low magnification ESEM image of the latex surface highlighting irregularities and defects.

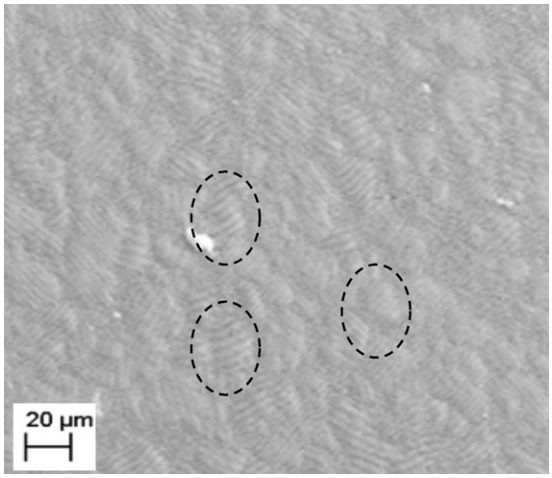

Fig. 9. ESEM image showing the crystalline appearance of the latex surface. Some of the what are described as individual grains have been highlighted.

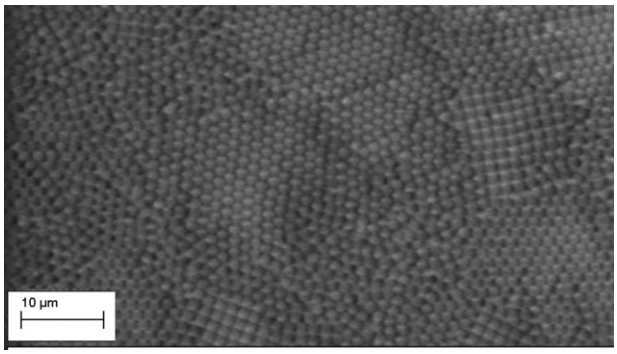

Fig. 10. High magnification ESEM image of the structure of the studied latex showing different packing arrangements.

4. Conclusions

Environmental scanning electron microscopy has yet again been shown to be a useful tool for the study of the microstructural evolution of drying latex films. The approach that we adopted for this study differs when compared to those used in previous ones, which were predominantly aimed at examining surface drying mechanisms in situ [10,13,15]. Here, by allowing the latex to initially film form, we have been able to make observations and conclusions regarding the structural development of the specimens under investigation not only in 2D, but also in 3D. This was achieved by examining the layering of particles in the cracks that were naturally formed during drying. The observations clearly confirmed that colloidal systems dry using a combination of both horizontal and vertical mechanisms. Furthermore it was also shown that, following film formation, the specimen can undergo what has previously been described as a subsequent aging process during which morphological changes can take place leading to changes in the properties (e.g. tensile strength) of the latex system [24]. Here, it is suggested that the ageing process should not only be associated to migration of surfactants, as previously suggested [24], but also with the formation of additional defects and/or irregularities. Finally, it was demonstrated that during film formation particle packing yields HCP, SCP and random arrangements which include surface defects. Further, ESEM examination revealed that these combined arrangements resulted in the formation of a crystal like structure in the latex. Therefore, based on the experimental observations presented in this study, it can be suggested that some modifications to the latter stages of the film formation mechanism taking place at $T < T_g$ of the latex can be considered. Firstly the close packing of particles, as suggested above, can be achieved via different arrangements. Therefore it would be expected that in areas where two arrays of differently packed particles, say HCP and SCP, are forming next to each other, a zone of randomly packed particles will naturally be created. This zone, consisting of randomly packed particles and voids would act as a boundary, between the two arrays and may also trigger the formation of other similar structures. This will ultimately result in the creation of a weak crystal-like structure of the type observed in the present study.

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