Macromol. Symp. **2009**, 281, 119–125 DOI: 10.1002/masy.200950716

Latex Film Formation in the Environmental Scanning Electron Microscope

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Summary: Environmental scanning electron microscopy (ESEM) was used to study the film formation mechanisms and extent of coalescence of three acrylic latex compositions with different glass transition temperatures (T_g), here defined as standard-low T_g, standard-high T_g (both carboxymethyl cellulose- stabilised) and novel (stabilised with a novel polysaccharide derived from agricultural waste). The ESEM analysis revealed that the microstructure of the standard – low-T_g system consisted of individual particles in dispersion and upon evaporation a continuous film formed, whereas in the case of the standard - high T_g latex particle deformation was not observed, but particle aggregation resulted in the formation of crystal-like structures that have formed via the formation of stacking faults. However, in the case of the novel system the microstructure consisted of individual particles and clusters and during evaporation a discontinuous film formed with voids present within its structure and some of the clusters accumulating on the surface of the specimens.

Keywords: ESEM; film formation; polymer latex

Introduction

Polymer latices, with their wide range of applications, have been the subject of many theoretical and experimental studies. When used for its traditional applications, i.e. as paint or adhesive, the latex is applied in its wet state to a surface and allowed to dry and form film under ambient conditions. Therefore, conventional electron microscopy, with its extreme drying and sample preparation requirements, will not be suitable for the examination of latices in their natural wet state. On the other hand, environmental scanning electron microscopy[1], which offers the possibility of imaging 'wet' and insulating specimens, has been successfully used in the study of a number of systems and dynamic processes including latices and film formation.[2–6]

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.[4] In this way, the chamber can be held at pressures usually in the range of 1–10 Torr[7], while the gun and column remain at pressures of $\sim 7.5 \times 10^{-7}$ Torr. Moreover, by using a correct pumpdown procedure[8] and by controlling the temperature of the specimen, which in the ESEM is usually done by using a Peltier stage, dehydration 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[8] and by increasing the temperature of the specimen or reducing the chamber pressure, it is possi-

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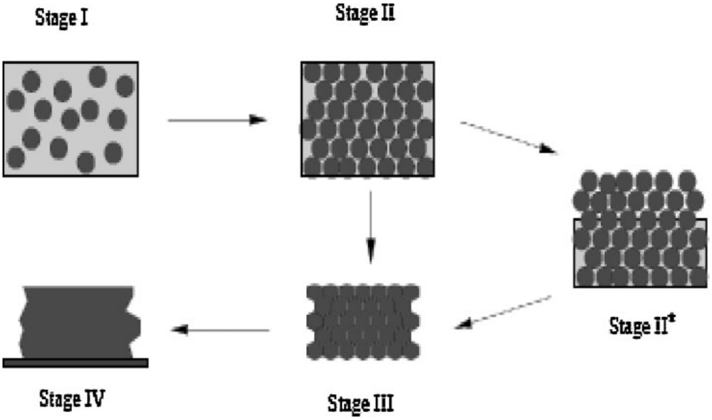

Figure 1.
Schematic representation of an idealized film formation process. Adapted from Keddie *et al.* to include the intermediate Stage II*.

ble to produce evaporation conditions within the specimen chamber, which allows examination of the process of film formation.

As mentioned above, polymer latices are important industrial products and the subject of many research studies. Latex, which is an example of a wet insulating material, can be defined as a colloidal suspension of spherical polymer particles with varying diameters. When water is allowed to evaporate from the system, the aqueous suspension undergoes a series of transformations, which result in the formation of a continuous dry polymer film. This process, known as film formation, contains four main stages that can be described as follows:[9–17] Stage I – dispersed suspension of polymer particles; Stage II – concentrated suspension of particles in contact with each other, surrounded by solvent-filled interstices; Stage III – ordered array of deformed particles; Stage IV – a molecularly continuous and homogeneous film formed as a result of polymer interdiffusion.

In 1995, Keddie *et al.* [4] used environmental scanning electron microscopy (ESEM) 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.[9–17] The stage, defined as II*, is characterized by a randomly packed array of deformed particles which still contain water-filled interstices. A schematic representation of the process is shown in Figure 1.

More recently, Keddie *et al.*[18,19] 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 this paper we present the results from an ESEM investigation into the film formation mechanisms of novel acrylic latex, which has been stabilised by using a new polysaccharide, derived from agricultural waste, and two standard polymer systems, where the conventional carboxymethyl cellulose (CMC) has been used as a stabiliser. The novel polysaccharide consists of a number of monosaccharides (including arabinose and xylose) formed from five- and six-membered rings and has a low molecular weight, only a few thousand a.m.u.s rather than the hundreds of thousands found in cellulose for example. The polysaccharide also contains a significant amount of interfacially active protein ~15%. It is suggested that the initial latex particle stabilization comes from the protein component and ultimately the polysaccharide component stabilises the latex particles by adsorbing on their surface, rather than by chemically grafting on the growing polymer particles, which is the case for the conventionally used CMC. Initial examinations[20] have indicated that the novel latex can form film without the addition of coalescing solvents, which, as suggested above, on one hand would provide an alternative method for the production of VOC-free architectural coatings and, on the other, would comply with the stringent EU and DEFRA regulations.[21]

Materials and Methods

Three aqueous latex compositions, supplied by ICI Plc, based on copolymers of methyl methacrylate (MMA) and 2-ethylhexyl acrylate (2-EHA) were studied. In this paper the latices stabilised with carboxymethyl cellulose (CMC) will be referred to as standard-low and high T_g; the other stabilised with the new polysaccharide as novel. The three latices were initially about 55 wt% polymer. The glass transition temperatures (T_g) of latices were determined by differential scanning calorimetry (DSC), carried out on dry specimens, using a Perkin Elmer Pyris 1 instrument. The measured temperatures were 274 K for the standard-low T_g, 328 K for the standard-high T_g and 280 K for the novel latex.

The microstructural analysis was carried out on an FEI XL-30 environmental scanning electron microscope equipped with a Peltier stage. Wet samples from the above formulations were placed onto the cooling stage in the microscope chamber at a temperature of ca. 274 K. An evaporation-inhibiting pumpdown sequence was then performed, with the ambient air progressively replaced by water vapour. Once the purging cycle was completed, water vapour pressures and working distances of 3.5–4.5 Torr and 9.5–11.5 mm were set, which provided optimal imaging environments, i.e. sufficient resolution and minimal beam damage. Imaging of the specimens was carried out at an accelerating voltage of 10 kV. Increasing the temperature of the specimens by 1 or 2 degrees above the starting temperature of 273 K, as explained above, resulted in further dehydration of the latices, which allowed examination of the process of film formation.

Results and Discussion

Prior to considering the results from the ESEM examination, it is important to note that when we refer to latices as being 'wet', some water has in actual fact been removed from the surface of the specimens in order to obtain better quality images. Keddie *et al*.[1,4] used a similar approach in the study of latex film formation by means of ESEM. It was found that despite the fact that some of the surface water had been removed, the bulk of the samples remained 'wet'.

Standard Latex – low T_g

From the ESEM images of the standard-low T_g latex (Figure 2), it can be seen that under 'wet' conditions (Figure 2a) the microstructure of the specimen consists mainly of randomly distributed individual particles with an average size of ca. 300 nm. Due to the fact that some of the water has already been removed, as explained above, some of the polymer particles are in contact. Despite that, they are still physically distinct, i.e. no significant deformation has occurred, and therefore it can be concluded that the latex is in Stage II/II*. By increasing the temperature of the specimen (Figure 2b), water evaporation takes place, which resulted in the formation of a continuous polymer film. However, due to the fact that not all particles have lost their identity and boundaries are still clearly visible, it can be concluded that under these conditions the latex is in Stage

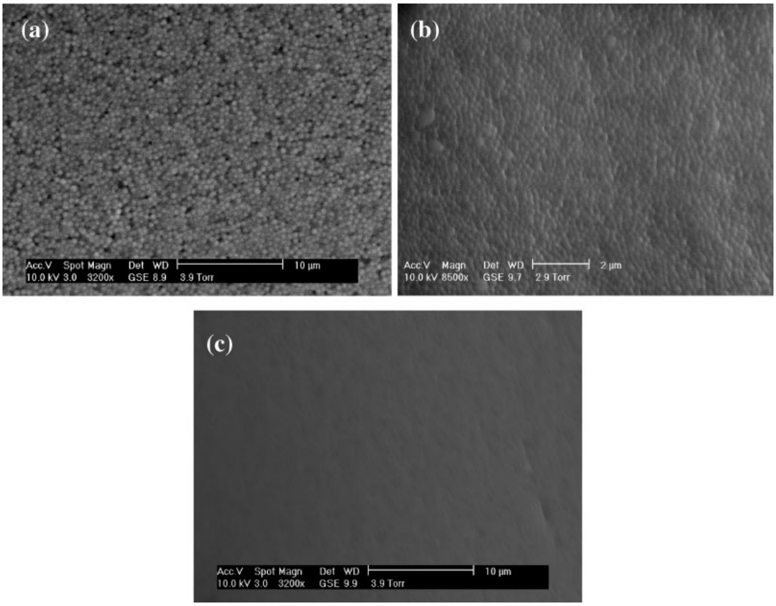

Figure 2.
ESEM images of a standard-low T_g latex specimen during film formation; (a) $T = 273$ K, (b) $T = 275.5$ K, (c) $T = 277.5$ K.

III/IV. In the final Stage IV (Figure 2c) all particles appear to have lost their identities and only topographical features due to defects and/or impurities can be seen within the structure of the polymer film. Based on the above results, which are comparable to those obtained in previous studies[1–5], it can be said that the film formation mechanism of the standard-low T_g acrylic latex is in a good agreement with the conventional descriptions.

Standard Latex – High T_g

The ESEM results for the film formation mechanism of the standard-high T_g latex are presented in Figure 3. The structure of the latex at the early stages of the drying process is similar to the standard–low T_g latex and consists of individual randomly distributed polymer particles in contact with each other. However, due to the fact that the glass transition temperature of the latex is much higher than the temperatures

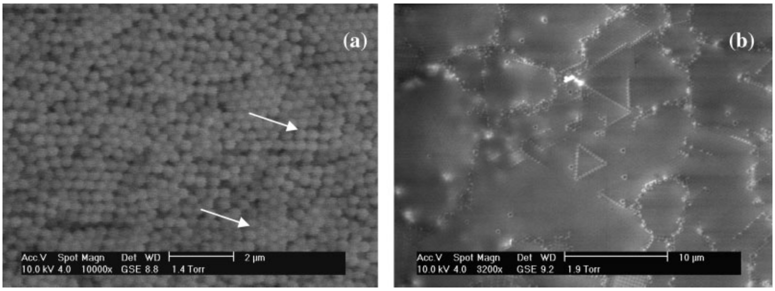

Figure 3.
ESEM images of standard–high T_g latex during drying; (a) in the intermediate stages ($T = 276$ K) of film formation particles form arrays (indicated by arrows) with hexagonal and four-fold symmetry; (b) at lower magnifications grain boundaries and stacking fault defects are clearly seen within the structure of the specimen.

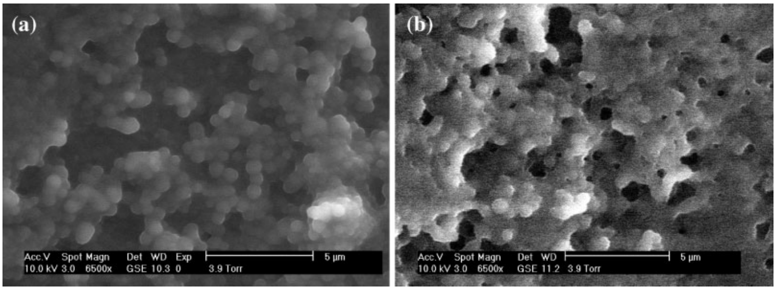

Figure 4.
ESEM images of novel acrylic latex at (a) $T = 274$ K and (b) $T = 276$ K.

at which film formation was observed in the ESEM, it was found that upon drying the particles did not deform and/or coalesce, but formed well-ordered arrays. The end result was the formation of a colloidal crystal, within the surface plane of which the majority of the packing was found to have hexagonal symmetry, although occasionally four-fold symmetry was also observed (Figure 3a). At lower magnifications (Figure 3b) the packing is seen to have many defects, both in terms of 'missing' particles and in terms of grain boundaries where the orientation of the planes changes.

Novel Latex

The results for the film formation mechanism of the novel acrylic latex are presented in Figure 4 (a, b). It is clearly seen that under 'wet' conditions (Figure 4a) the microstructure of the specimen consists of individual particles and clusters with sizes in the range 2–5 µm. The presence of these clusters was also confirmed by particle size measurements carried out by ICI Plc using a Coulter LS230 light scattering apparatus. Due to the fact that the spherical particles with diameters of ca. 300 nm are still physically distinct, i.e. no significant coalescence has taken place, it can be said that the latex is in Stage II/III of the film formation process.

Figure 4b reveals the microstructure of the specimen at a temperature of 276 K. It is evident that at this temperature, significant water evaporation has taken place, which has resulted in the formation of a discontinuous film with voids present within its structure. The fact that not all particles have completely lost their identities, suggests that the latex is in Stage III/IV.

Due to the fact that imaging of the latex specimens was carried out below their T_g of 280 K, it is somewhat surprising to observe the latter stages of film formation. However, it is suggested that as the microstructural analysis was carried out at temperatures very close to the minimum film formation temperature ($T = 278$ K), partial particle deformation and coalescence, possibly helped by water plasticization, would naturally be expected to take place.

The discontinuity of the film can be explained by taking into consideration the varying shapes and sizes of the clusters. During water evaporation, i.e. when clusters and individual particles come into contact, it is obvious that voids within the polymer film could easily form. Therefore, based on the experimental evidence it appears that the film formation mechanism of the novel latex is somewhat different to the conventional descriptions, because of the presence of clusters in the latex system.

Moreover, as seen in Figure 5, in the final stages of the film formation process, a number of clusters appear to remain on the surface of the film. In the ESEM image the clusters appear brighter than the rest of the polymer film. This is believed to be caused by a difference in the working distance; i.e. the distance between beam exit point and cluster is shorter than the distance between beam exit point and polymer film.

The accumulation of clusters on the surface of the latex specimens can be

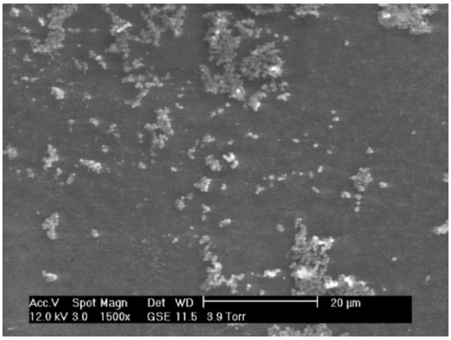

Figure 5.
Low-magnification ESEM image of a novel acrylic latex specimen in the final stage of the film formation process, showing accumulation of clusters on the surface of the drying film.

explained by taking into consideration the Peclet number for latices.[22,23] For a latex system the Peclet number can be defined as:

$$Pe = \frac{HE}{D},$$

where H is the film thickness (m), E is the evaporation rate (m/s) and D is the diffusion coefficient (m^2/s). The literature suggests that if $Pe \sim 0(1)$ then no surface accumulation is to be expected, but if $Pe >> 1$ then diffusion is weak and the particles will accumulate at the top of the surface during drying. D is taken as the Stokes-Einstein diffusion coefficient:

$$D = \frac{kT}{6\pi\mu R}$$

Taking μ as water viscosity - 10^{-3} Ns/m^2, kT as 4×10^{-21} J and E as 3×10^{-8} m/s then,

$$Pe \sim 10^{11}\, H\, R,$$

with both H and R in metres. Hence, if R (in this case the size of a cluster) is 5×10^{-6} m then to get uniform films, H has to be $\leq 2 \times 10^{-6}$ m. Therefore, for the typical sample film thickness, which is in the range of $\sim 200\,\mu$m, surface accumulation will be expected, which is in agreement with the experiments.

Conclusion

Environmental scanning electron microscopy (ESEM) has proven to be a successful method for studying the process of the evolution of aqueous polymer dispersion into a dry film. The ESEM results revealed that there are differences in both the microstructures and the drying behaviour of the studied latex systems. The ESEM analysis revealed that the microstructure of the standard-low T_g system consisted of individual particles and upon evaporation a continuous film formed, whereas in the case of the standard-high T_g latex the particles did not deform and/or coalesce, but formed well-ordered arrays. However, in the case of the novel system the microstructure consisted of individual particles and clusters and during evaporation a discontinuous film formed with voids present within its structure. Furthermore, it was found that in the final stages of the film formation process some of the clusters accumulate on the surface of the latex specimens.

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