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Evaporation-driven Self-assembly of Binary and Ternary Colloidal Polymer Nanocomposites for Abrasion Resistant Applications

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ABSTRACT: We harness the self-assembly of aqueous binary latex/silica particle blends during drying to fabricate films segregated by size in the vertical direction. We report for the first time the experimental drying of ternary colloidal dispersions and demonstrate how a ternary film containing additional small latex particles results in improved surface stability and abrasion resistance compared with a binary film. Through atomic force microscopy (AFM) and energy-dispersive X-ray spectroscopy (EDX), we show that the vertical distribution of filler particles and the surface morphologies of the films can be controlled by altering the evaporation rate and silica volume fraction. We report the formation of various silica superstructures at the film surface, which we attribute to a combination of diffusiophoresis and electrostatic interactions

between particles. Brownian dynamics simulations of the final stages of solvent evaporation provide further evidence for this formation mechanism. We show how an additional small latex particle population results in an increased abrasion resistance of the film without altering its morphology or hardness. Our work provides a method to produce water-based coatings with enhanced abrasion resistance as well as valuable insights into the mechanisms behind the formation of colloidal superstructures.

KEYWORDS: Latex film formation, stratification, evaporation driven self-assembly, ternary dispersions, silica nanoparticles, abrasion resistance, Brownian dynamics.

INTRODUCTION

The drying of latex films is a facile and inexpensive coating technique in which dispersions containing colloidal polymer particles are dried to form solid films¹. These colloidal films have a wide variety of applications, including paints², inks³, adhesives⁴, and cosmetics⁵.

Vertical self-assembly of colloidal particles during drying was initially linked to the formation of solid skins at the liquid/air interface. Routh and Russell showed that skin formation can be predicted by considering two different mechanisms: the evaporation of water and the diffusion of colloidal particles⁶. The competition between these mechanisms in a film of height H can be quantified by means of the Péclet number, $Pe = H\dot{E}/D$, where $\dot{E}$ is the evaporation rate and D is the diffusion coefficient. When $Pe \gg 1$, evaporation is dominant. In this situation, the diffusion of particles is too slow in relation to the evaporation, causing the particles to become trapped at the receding interface and resulting in skin formation. Conversely, when $Pe \ll 1$, diffusion is more rapid, and particles remain uniformly dispersed throughout the film^{6,7}.

Recently, it has been suggested that the drying of binary colloidal films may be a promising single-step method for the fabrication of films containing two layers^{8,9}. These multi-layered films are highly desirable in applications such as antibacterial coatings¹⁰, anti-reflective coatings¹¹, organic photovoltaics¹², and inkjet printing¹³. Trueman *et al.* proposed that drying a binary mixture containing particles with Péclet numbers either side of unity should result in self-stratification^{14,15}. This was achieved by using two different particle sizes. Larger particles become trapped at the surface while the smaller particles diffuse freely below.

Fortini *et al.* later showed experimentally and in Langevin dynamics simulations that small-on-top stratified films could be formed by drying binary dispersions in which both Péclet numbers were greater than one, $Pe_L > Pe_S > 1$, where the subscripts S and L designate small and large particles¹⁷. This film architecture was explained by considering the concentration gradient of particles through the height of the film. The difference in concentration results in an osmotic pressure gradient, which forces particles away from the liquid/air interface. This mechanism is known as diffusiophoresis¹⁸ and has a greater effect on larger particles, resulting in a small-on-top film structure. Further insights on this phenomenon was provided by Sear and Warren¹⁸.

Zhou *et al.* developed a model (ZJD model) that could predict which stratification effect would be observed¹⁹. Their model produced two conditions to be satisfied for stratification to be observed: $Pe_L > 1$ and $\alpha^2(1 + Pe_S)\phi_S > C$, where ϕ_S is the volume fraction of small particles, α is the size ratio between the particles (large/small), and C is a constant close to 1. To achieve small-on-top stratification, larger Péclet numbers and higher volume fractions of the small particles are required. However, the ZJD model does not consider the influence of diffusiophoresis, which can result in inaccurate predictions compared with experimental tests.

Simulations of drying particle blends were extended further by Fortini and Sear to include ternary and polydisperse mixtures²⁰. Their Langevin dynamics simulations showed that the particle size distribution changes through the height of the film, with larger particles at the bottom while the surface is enriched with smaller particles. Cusola *et al.* reported similar experimental results when drying polydisperse systems²¹. To our knowledge, no experimental studies have reported on the drying of ternary latex blends to form stratified films.

Nanocomposite films can be easily fabricated by drying blends of latex and inorganic particles – known as filler particles²²⁻²⁴. A common example of this is the use of pigments in paints which are combined with the film-forming polymer to create coloured coatings²⁵. The addition of filler particles can alter or impart many other properties, including antimicrobial properties²⁶, electrical conductivity²⁷, or mechanical properties, such as hardness and tensile strength²⁸. Filler particles used to improve mechanical properties are known as reinforcing particles²⁹.

Silica nanoparticles are a popular choice for use as reinforcing particles in composite polymer materials. It has been shown that silica-containing composites exhibit an increased elastic modulus³⁰, yield stress³¹, hardness, and scratch resistance³². Conventional sol-gel methods for producing polymer/silica composites involve the use of tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS), both of which are relatively expensive and can result in the release of volatile organic solvents (VOCs)³³. A simple and greener alternative is the drying of latex blends containing colloidal silica. Several publications focus on the creation of latex/silica nanocomposite films by drying latex dispersions containing silica^{22,33-36}. Martinez and Lewis, and Yang *et al.* studied the film forming behaviour and mechanical properties of latex films containing colloidal silica particles^{33,35}. Meanwhile, Grillet *et al.* and Kobayashi *et al.* investigated the influence of silica on film morphology and polymer interdiffusion^{22,34}. The aim

of these studies was the fabrication of homogeneous films with evenly dispersed silica particles. There is very little in the literature on the self-assembly of silica particles during drying to achieve vertical segregation. Liu *et al.* and Luo *et al.* studied the stratification in latex blends containing silica, however their focus was on the self-assembly mechanisms rather than the benefits of silica as reinforcing particles^{37,38}. Their research was also limited to the study of binary colloidal blends.

In composite coatings or films, it is beneficial to control the vertical distribution of the filler particles. There are many examples where it is highly desirable for them to only be positioned at the top surface, as opposed to throughout the whole film. This is the case for bactericidal nanofillers, which need to be at the film surface to impart antimicrobial activity³⁹. Recently, Dong *et al.* harnessed the stratification process to fabricate antibacterial coatings with an optimized zinc oxide coverage at the surface⁴⁰. Reinforcing particles are also primarily required at the surface of polymer films to improve hardness. Nunes *et al.* showed that the stratification of hard nanolatex particles improved surface hardness as well as anti-blocking and fat resistance⁴¹. Similarly, the hardness and abrasion resistance imparted by silica nanoparticles are primarily required at the film surface. Moreover, being hard particles, the silica particles do not deform during the film formation process³⁵. This can result in porosity, which can have a detrimental effect on mechanical properties⁴². Reinforcing particles can also result in a decrease in strain at failure when located in the bulk of the film⁴³. Therefore, the self-assembly of large latex and small silica particles presents an alternative method to create a stratified abrasion resistant coating through a single-step process³⁹. However, stratified layers containing only silica are expected to have poor stability, resulting in inadequate abrasion resistance. We show here that ternary latex blends containing additional small latex particles can be utilised to resolve this

issue. The resulting surface contains both silica and latex. The softer latex particles can deform during drying, creating a surface with enhanced mechanical properties and improved stability.

Here, we describe experiments and simulations investigating self-assembly during drying of binary and ternary colloidal dispersions, with the aim of enriching the film surface with both silica nanoparticles and smaller latex particles. We show how this architecture enhances the abrasion resistance of the film, while also maintaining surface stability. Overall, our work demonstrates that ternary colloidal blends can be used to fabricate abrasion resistant films through a simple and cost-effective method and provides a tool for the development of better performing and more durable functional coatings.

EXPERIMENTAL SECTION

Materials. Two latex samples with different particle sizes were prepared by emulsion polymerisation. Both latex samples contained waterborne particles of poly(butyl acrylate-co-methyl methacrylate) (P(BA-co-MMA), 1:1 by weight). The large latex particles were obtained by surfactant-free seeded emulsion polymerisation, using 1 wbm% sodium styrene sulfonate (NaSS) as a stabiliser. A description of the synthesis is provided elsewhere⁴⁴. The smaller latex particles were synthesised by microemulsion polymerisation using sodium dodecyl sulfate (SDS) as a surfactant and ammonium persulfate (APS) as an initiator. LUDOX® TMA aqueous silica nanoparticle dispersion was obtained from Sigma-Aldrich and used as received. These silica nanoparticles are modified with negatively charged aluminate groups to improve stability in water of pH 4-10.5. The average particle diameters of the large latex, small latex and silica dispersions were 232 nm, 56.3 nm and 24.5 nm, respectively (determined by dynamic light scattering, see SI Figure S1). The zeta potential values of the large latex, small latex, and silica particles were -42.9 mV, -25.2 mV, and -33.9 mV, respectively (measured using electrophoretic

light scattering). All values being below -20 mV indicated that the particles were stable within the dispersions.

Latex Film Preparation. Composite latex films containing silica were prepared by casting and drying colloidal dispersions on glass substrates. Both latex and silica dispersions were diluted to 10 wt% solids content using deionized water. Before mixing the dispersions, the silica was placed in a sonication bath for 10 minutes to minimise any aggregation. The latex and silica dispersions were then blended together at different ratios to obtain silica volume fractions (in the initial wet films) of $\phi_{Si} = 0.007, 0.013$ and 0.019 . The resulting silica volume fractions in the dry films were $\phi_{Si} = 0.06, 0.17$, and 0.29 , respectively. The exact mixing ratios can be seen in Table S1 in the SI.

Binary latex/silica films were cast by depositing 400 μ l of these mixed dispersions onto square glass slides (18 mm $\times$ 18 mm), which had previously been cleaned with acetone and a UV ozone cleaner. The resulting initial film height was estimated at around 1.2 mm. Control latex samples were also created by casting 400 μ l of dispersion containing only large latex. The films were dried under three different conditions to provide a wide range of evaporation rates. Slow evaporation rates were achieved by drying in a high humidity environment, created by heating deionised water at 50 °C within a semi-sealed glass container. The humidity was >90 % RH throughout the film drying process, which could take up to 7 days. A hot plate was used to increase the evaporation rate, drying the films in about 15 minutes. The temperature of the substrate was measured over the drying period using a thermocouple. A graph of this temperature profile is shown in the SI in Figure S2. Films were also dried at room temperature (21 ± 1 °C, 50 ± 5 % RH) for 10 hours to provide more moderate evaporation rates. The fast,

moderate, and slow evaporation rates were estimated at $1.4 \times 10^{-6} \text{ m s}^{-1}$, $1.1 \times 10^{-7} \text{ m s}^{-1}$, and $3.2 \times 10^{-9} \text{ m s}^{-1}$, respectively ⁴⁵.

Ternary dispersions were created by adding the small latex to the mixed dispersion of silica and large latex. The dispersions were mixed to give a final volume ratio (in the dry films) of 15:15:70 (silica : small latex : large latex). Binary control samples, containing only the two types of latex, were also prepared. The volume ratio for these films was 30:70 (small : large). Following drying, some ternary films were annealed in an oven at 80 °C for 4 hours.

Atomic Force Microscopy (AFM). AFM measurements were performed using a NanoWizard[®]3 from JPK Instruments. Quantitative Imaging[™] (QI) mode was used to produce topographic images and measure nanomechanical properties. All samples were probed using silicon cantilevers (NSG01 or NSG30 Series by NT-MDT, depending on sample hardness) with typical springs constants of 5.1 N/m or 40 N/m and a tip radius of 6 nm. Images were captured using a resolution of 256×256 pixels. AFM images were processed using JPK Data Processing software.

In QI mode, force-distance curves are produced for each pixel in the topography image. An estimate of the local elastic modulus can be calculated from the force curves by applying the Derjaguin-Müller-Toporov (DMT) model⁴⁶. For parabolic indenters, this model takes the form⁴⁷:

$$F - F_{adh} = \frac{4E\sqrt{R}}{3(1-\nu^2)}\delta^{3/2},$$

where F is the force, F_{adh} is the adhesion force that occurs during tip retraction, E is the elastic modulus, R is the tip radius, δ is the indentation, and ν is the Poisson ratio of the sample.

Using the data processing software allowed all force curves within an image to be batch processed. The elastic modulus was calculated for each pixel of the AFM image to allow the production of elastic modulus maps. Due to the large difference in modulus between latex and

silica particles, the two phases could be easily distinguished in these images. In addition, the magnification and resolution of the images were controlled such that silica nanoparticles observed within the images has a size greater than 1 pixel, thus making it possible to distinguish between the two phases in elastic modulus maps (Figure S3 in the SI). Image analysis software (ImageJ) was used to calculate the silica surface coverage from the images. Six different areas from two identical samples were averaged for each of the different conditions to provide a representative value of silica surface coverage. The heights of the surface microstructures were also calculated by taking an average of the maximum heights from each of the six areas.

Energy-dispersive X-ray Spectroscopy (EDX). The chemical composition of the film surfaces was analysed using EDX (JEOL JSM-7800F FEG-SEM). The silicon concentration was measured to provide an indication of silica surface content. Samples were coated with a gold/palladium alloy before analysis, and relatively low accelerating voltages (5 keV) were used to minimise charge accumulation and sample damage. 5 different regions were analysed to produce an average for silica surface content for each sample.

Water Contact Angle (WCA). A drop shape analyser (KRÜSS DSA100) was used to measure water contact angles on the film surfaces. 3 µl droplets of deionized water were used. Averages and standard deviations were calculated from six WCA measurements per sample.

Abrasion Testing. Latex films were subject to abrasion tests compliant with BS EN 1096-2 and ISO 9211-4, carried out using a reciprocating abrader (Taber Industries Model 5900). Tests were carried out at a rate of 50 cycles per minute for 1-2 minutes using a felt pad as abrasion material. Forces of 1-2 N were applied.

Hardness Testing. Hardness tests were carried out under ambient conditions using a Vickers hardness tester (Struers Durascan-70). A relatively small load (10 g) was used to avoid

indentation into the hard glass substrate below. Twenty indentations were made in a diagonal line across the samples to ensure that the obtained values were representative of the whole sample.

SIMULATION SECTION

Previous literature suggests that particles are segregated by size during drying due to diffusiophoresis¹⁷⁻¹⁹. To simulate the last stages of solvent evaporation and surface structure formation, we perform Brownian dynamics simulations of a drying system containing $\mathcal{N}$ small particles suspended above a pre-packed bed template of larger particles – in other words, we solve $\mathcal{N}$ coupled Langevin equations in the over-damped limit.

The small particles, with diameter d , are randomly initialised in the upper 2/3 of the system without overlap⁴⁸. In order to simulate Brownian motion, a random velocity is generated for each particle by sampling from a Gaussian distribution with standard deviation $\xi = \sqrt{2D_0 dt}$, where dt is the Brownian time-step and D_0 is the bare diffusion coefficient, hereafter set equal to 1. The system is confined between two parallel horizontal walls perpendicular to the z -axis. The upper wall represents the liquid/air interface, while the lower wall indicates the point below which the larger particles are assumed to have formed a homogeneous densely packed structure. Periodic boundary conditions are applied along the x and y -axis to avoid any boundary effects caused by the finite size of the model. $\mathcal{M}$ large particles (with diameter D) are placed on top of the lower wall and act as the top layer of the densely packed latex, remaining fixed during the whole simulation. The upper wall descends over time, representing the falling liquid/air interface as evaporation occurs. The wall moves with constant velocity, descending from position $z_0(0)$ to $z_0(t_f)$ in the time lapse t_f . The system can then evolve up to time t_{tot} .

The small suspended particles are modelled as interacting via a 12-6 Lennard-Jones potential of the form:

$$U_{ss}(r) = 4\varepsilon_{ss} \left[\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 \right],$$

where ε_{ss} defines the attraction strength between small particles and r is the distance between the centres of the particles. These interactions are considered when they are separated by less than $2.6d$ ($U_{ss}(2.6d) \approx -1.3\%\varepsilon_{ss}$). Experimental findings demonstrated that the larger particles in our system exhibited stronger (more negative) zeta potential values. The interactions between large and small particles are therefore given by the repulsive part of the Lennard-Jones potential of the form:

$$U_{Ls}(r) = 4\varepsilon_{Ls} \left[\left(\frac{\Sigma}{r} \right)^{12} - \left(\frac{\Sigma}{r} \right)^6 \right],$$

where $\Sigma = d/2 + D/2$. Interactions between large and small particles are considered when they are separated by less than $2^{1/6}\Sigma$ (corresponding to the location of the minimum of U_{Ls}). It is assumed that there is a large concentration of large particles below the lower wall. The interaction between this wall and the suspended particles is therefore modelled using repulsive force of the form:

$$F(z, t) = \left(\frac{\sigma_w}{|z - z_0(t)|} \right)^{30} - 1,$$

if $|z - z_0(t)| < \sigma_w$ (otherwise $F(z, t) = 0$), where σ_w defines the softness of the wall and $z_0(t)$ is the position of the wall (for the lower wall $z_0(t) \equiv 0$). The upper wall exerts the same force, but in the opposite direction.

In order to study two of the experimental cases (at slow and fast evaporation rates), we initialise the position of the $\mathcal{M}$ large spheres in two different ways. In the first case we place the particles in a hexagonal closed packing structure. This case simulates a slow evaporation rate,

where large particles have more time to relax and form a close-packed structure. The second case represents a fast evaporation rate. In the latter, we let the large spheres fall randomly on the bottom of the box. If a particle falls on top of another, the two remain there stuck together at a distance D apart.

The following parameters have been used for both cases: the prefactor which determines the interaction strength between small particles, $\varepsilon_{ss} = 1.2k_B T$, where $k_B T$ is the thermal energy. This value was chosen so that the small particles aggregate, i.e. so that the temperature is below the temperature of the critical point value for the small particles⁴⁹. For interactions between large and small particles, $\varepsilon_{LS} = 5k_B T$, although the precise value is negligible, since we truncate $U_{LS}(r)$ at the minimum. The key feature in our choices of parameters is that the small particles aggregate, preferring to be in the vicinity of their own kind rather than the large particles. The diameters of the large and small particles (D and d , respectively) were related by the equation $d = 0.1D$, such that the size ratio was similar to that used in the experiments. The wall softness, $\sigma_w = 0.15D$. The dimensions of the base of the simulation box were $4D \times 5.2D$ with the height varying depending on the case that was chosen (see below). The Brownian timestep, $dt = 10^{-4}\tau$, and the number of large particles, $\mathcal{M} = 24$. All times are given in units of $\tau = d^2/D_0$. The remaining variables are set to different values depending on the case.

Case 1: slow evaporation. Here the number of small particles was $\mathcal{N} = 4000$ such that the volume fraction was similar to the experimental results. The initial and final upper wall positions were $z_0(0) = 5D$ and $z_0(t_f) = 1.25D$, respectively. The initial value was chosen to provide space for the small particles to be initialised between the wall and the latex structure below. The final value corresponds to the point in time when the small particles are well-packed onto the

larger particle structure. The time taken for the wall to descend to this point, $t_f = 187.5\tau$, and the system was allowed to evolve until $t_{tot} = 750\tau$.

Case 2: fast evaporation. Here the large latex particles are more spread out, inhabiting a larger volume. As such the number of small particles was increased to $\mathcal{N} = 15000$, so that the final volume fraction of the small particles was of the same order. We also set $z_0(0) = 10D$, $z_0(t_f) = 3.15D$, $t_f = 62.5\tau$, and $t_{tot} = 250\tau$. These values were all altered since the latex structure had a larger height. The initial and final positions of the upper wall were therefore increased. The time taken for the wall to reach the latex structure was also different.

RESULTS AND DISCUSSION

We investigate the self-assembly of latex and silica particles in drying films to evaluate the potential positive impact of size segregation on their mechanical properties and surface stability. First, we investigate binary latex and silica blends with different silica concentrations dried at different evaporation rates. We then introduce another latex particle population to demonstrate that a ternary blend provides better abrasion resistance while retaining its mechanical properties.

Binary Latex/Silica Films. AFM was used to image the surfaces of binary latex/silica films. Figure 1 shows the topography images obtained when altering two variables: the evaporation rate and the silica volume fraction. We first consider films containing the lowest silica volume fractions ($\phi_{Si} = 0.06$). When dried at slow evaporation rates, the top surface consists of hexagonally packed latex particles, as seen in Figure 1(g). A small number of silica nanoparticles can be seen located at the interstices between latex particles. These same structures are still observed in Figure 1(h), when drying at moderate evaporation rates. However, increasing the evaporation rate further causes significant changes in the film surface. It can be seen in Figure 1(i) that the top surface now contains only small particles. Maps of the elastic modulus (shown in

the SI in Figure S3) indicate that these are all silica nanoparticles. Although the surface is clearly enriched by the silica particles, they do not form a homogeneous layer above the latex. Instead, grid-like superstructures are created. The cavities within the silica structures are of a similar size and shape to the latex particles, indicating that the silica is templated by close-packed latex structures below.

When drying films containing higher silica volume fractions ($\phi_{Si} = 0.17$ and 0.29) all of the resulting surfaces contain only silica. However, the exact superstructures formed by the silica particles vary considerably depending on the evaporation rate. Figure 1(d) shows the surface of a film containing a volume fraction of 0.17 dried at slow evaporation rates. The structure observed in this film displays a much higher degree of ordering when compare with the others. The holes in the superstructure form a clear hexagonal structure, similar to those reported by Utgenannt *et al.* in blends of latex and gold nanoparticles⁴⁵. Here, this is achieved using much lower evaporation rates.

Drying at moderate evaporation rates results in much more heterogeneous structures, with higher silica coverage, as seen in Figure 1(e). These structures more closely resemble those reported by Dong *et al.* in blends of latex and zinc oxide⁴⁰. Drying at even faster evaporation rates results in further alterations to the final silica superstructure. Figure 1(f) shows that the silica coverage is increased again, and the resulting surface is much smoother with a reduced number of cavities.

Figure 1. AFM topographic images of binary latex/silica films with different silica volume fractions (ϕ_{Si}), dried at slow, moderate and fast evaporation rates ($1.4 \times 10^{-6} \text{ m s}^{-1}$, $1.1 \times 10^{-7} \text{ m s}^{-1}$, and $3.2 \times 10^{-9} \text{ m s}^{-1}$, respectively).

Results showed that films containing a silica volume fraction of 0.29 displayed similar superstructures and trends to those observed when $\phi_{Si} = 0.17$. Although, with this higher silica volume fraction, the packing of silica particles appears to be more inefficient, resulting in significant height variations, as seen in Figure 3. Importantly, although the sample dried at slow

evaporation rates does still have grid-like structures in some regions, it also contains rough forest-like regions in which the silica does not pack uniformly between latex particles, as shown in Figure 2. This variation in structure was not observed for any other combination of evaporation rate and silica volume fraction.

Figure 2. AFM topography images of the binary latex/silica film with $\phi_{Si} = 0.29$ dried at slow evaporation rates. Image sizes are (a) 10 x 10 μm and (b-c) 3 x 3 μm .

Figure 2(a) also highlights the difference in height between different types of silica superstructure. In general, increases in either evaporation rate or silica volume fraction result in structures with greater heights, as seen in Figure 3. The greatest height was measured at 236 ± 26 nm and was achieved in films with the highest silica volume fraction ($\phi_{Si} = 0.29$) dried at the fast evaporation rate. Structures in films with the same silica volume fraction dried at moderate and low evaporation rates had heights of 86 ± 18 nm and 102 ± 76 nm, respectively. The standard deviation of the later scenario was much larger due to the two distinct structures that were present at the surface. The height of the grid-like and forest-like regions were 32 ± 17 nm and 172 ± 36 nm, respectively. As mentioned previously, the results also showed that the height

was affected by the silica volume fraction. The lowest height measured, for films which displayed small-on-top stratification, was achieved when $\phi_{Si} = 0.06$ (at fast evaporation rates). These structures had a height of only 23 ± 1 nm, indicating that only a single layer of silica particle protruded from the sample surface (given that the silica particle size is around 25 nm).

Figure 3. Graph showing the mean height of microstructures measured by atomic force microscopy (AFM) in latex films containing different volume fractions of silica, dried at different evaporation rates

Figure 4(a) shows the silica coverage, as calculated from AFM elastic modulus maps (Figure S3). The trends seen in the graph show good correlation with the AFM topography images. The samples with low silica volume fractions and slow-to-moderate evaporation rates have silica coverages of only 4.6% and 5.4%, which is to be expected as the majority of the surface consists of latex particles. In samples with the same silica volume fraction ($\phi_{Si} = 0.06$), but dried at fast evaporation rates, the silica coverage is increased greatly to nearly 50 %. This again matches the AFM topography images which show that the surface of this film is now enriched with the smaller silica particles. A similar trend is observed in films with $\phi_{Si} = 0.17$, with the silica

coverage increasing from $44 \pm 3\%$ to $66 \pm 6\%$ by increasing the evaporation rate. The value of silica coverage for the film with higher silica volume fraction ($\phi_{Si} = 0.29$) dried at moderate evaporation rates is the only value that does not match the AFM topography images. This can be attributed to the disordered packing of silica at the surface. The variation in topography caused by this has a slight effect on the elastic modulus images. The result is that silica particles that are at the surface but lower down than other parts of the surface may appear darker in the elastic modulus maps leading to a lower silica coverage measurement. This abnormal result is not observed when carrying out EDX analysis, which can be seen in Figure 4(b). Instead the EDX shows a clear trend between surface silicon concentration and evaporation rate at all silicon volume fractions.

Figure 4. Graphs showing the surface silica content of binary latex/silica films with different silica concentrations, dried at slow, moderate, and fast evaporations rates. Measured using (a) AFM and (b) EDX.

The silica superstructures formed when drying these binary dispersions have a strong impact on the wettability of the final film surface. Results indicate that both the silica and latex particles are hydrophilic, with all contact angles measuring below 90° , as shown in Figure 5. However, there is a large difference in contact angle among the different types of silica structures. The contact angle measured on the smoother surfaces of films with $\phi_{Si} = 0.17$ dried at fast evaporation rates (Figure 5(c)) is only $63 \pm 2^\circ$. Meanwhile, films containing silica superstructures with more holes and more heterogeneous height (Figure 5(b)) are slightly more hydrophobic, with water contact angles of up to $87 \pm 1^\circ$. It is possible that this change in wettability is caused by an increase in surface roughness⁵⁰, however it may also be affected by the degree of silica surface coverage.

Figure 5. (a) Water contact angle measured for binary latex/silica films containing different silica volume fractions dried at different evaporation rates, and (b-c) AFM images of corresponding film surfaces.

Formation of Silica Superstructures. In order to compare the experimental results to the those predicted by the ZJD model, the Péclet numbers were calculated for all three particles at each evaporation rate and can be seen in Table 1 (calculation methods shown in the SI). We find

that the results from these experiments match relatively well with the trends predicted by the ZJD model, reported by Zhou *et al.*⁶. Both showing that small-on-top stratification can be achieved by increasing either the silica volume fraction or the Péclet number (via increasing the evaporation rate). Furthermore, the model accurately predicts the stratification in all but one of the scenarios that were tested, as shown in Figure 6, with the exception being films dried at moderate evaporation rates with $\phi_{Si} = 0.06$. According to the model these films should form small-on-top structures, since the condition $\alpha^2(1 + Pe_S)\phi_S > 1$ is satisfied. However, experimental data shows that this does not occur, and the surface is made up predominantly of large latex particles. These results are similar to those obtained by Carr *et al.* which suggest that the ZJD model overpredicts small-on-top stratification^{51,52}.

As explained by Schulz and Keddie⁷, the ZJD model does make a few approximations leading to inaccurate predictions of some experimental results. For example, the solvent is modelled as being static, meaning that the flow past the particles during evaporation is neglected. In addition, the model only uses a second virial coefficient approximation for particle interactions, and these are for a hard sphere model rather than a DLVO model. Nevertheless, the experimental results do follow the general trends described by the ZJD model.

Table 1. Péclet numbers calculated for silica nanoparticles and both large and small latex particles at slow, moderate, and fast evaporation rates.

Particle	Péclet Number		
	Slow Evaporation	Moderate Evaporation	Fast Evaporation
Large Latex	2.1	71.1	189.6
Small Latex	0.5	17.2	45.8
Silica	0.2	7.4	19.6

Figure 6. State diagram for binary latex/silica films obtained from the ZJD model. The curve represents the equation $\alpha^2(1 + Pe_S)\phi_S = 1$, where the size ratio $\alpha = 9.5$. The line $Pe_L = 1$ (or $Pe_S = 1/\alpha$) is also plotted. Points are plotted for the different evaporation rates and silica volume fractions (in the wet state) that were used, and the experimental stratification that was observed is indicated by the symbol (+ or ×) as indicated in the key.

The results also show that larger evaporation rates enhance the stratification, resulting in larger concentrations of smaller particles at the surface. This effect can clearly be seen in Figure 1(f), when drying on a hot plate. This relationship can be explained by the thermal Marangoni flows, present in films dried at higher temperatures. Chen *et al.* suggest that drying dispersions on heated substrates can result in a three-stage lifetime consisting of inward flow, multi-cellular flow, and outward flow⁵³. The combined effects of these three flows may result in an enrichment of small particles at the final film surface. Moreover, the decreased viscosity of water at higher

temperatures could result in a synergic effect, enhancing the ease of diffusion for all colloidal particles.

The forms that the silica structures take are slightly more difficult to explain. Utgenannt *et al.* proposed that nanogrid superstructures form as a result of small particles being swept up through the interstitial spaces between larger particles⁴⁵. It was suggested that this was due to the high evaporation rates that were used ($\sim 2 \times 10^{-6} \text{ ms}^{-1}$). Here, nanogrid-like structures are reported at much lower evaporation rates, suggesting that other mechanisms are possible. Also, the size ratio between large and small particles is much smaller here (9.5 compared with 33.8) meaning that the small particles likely have reduced mobility compared with the nanoparticles used by Utgenannt *et al.* It is therefore more unlikely that these superstructures are formed only as a result of small particles being swept up through the latex structure. Instead, we explain the superstructures by considering diffusiophoresis as well as interactions between particles.

Previous literature has shown that two differently sized particles will separate vertically via diffusiophoresis¹⁷⁻¹⁹. We suggest that at this point the latex particles start to form a close packed structure, with the silica particles still above, at the liquid/air interface. As the surface continues to descend, the silica particles must come to rest on top of the latex. It is clear from the AFM images in Figure 1 and 2 that the silica particles first start inhabiting the interstices between latex particles. Further particles then build up within these voids creating taller superstructures, extending above the latex particles.

We suggest that this occurs due to the interactions between latex and silica particles. DLVO theory states that the two most important particle interactions that must be considered for colloidal dispersions are attractive van der Waals forces and repulsive electrostatic forces^{1,54}. Electrophoretic light scattering showed that the silica particles had weaker zeta potential values

than the latex (-33.9 mV compared with -42.9 mV) indicating that the latex particles have a stronger negative charge on their surface. It can therefore be concluded that the silica particles are subject to stronger repulsive electrostatic forces from the latex particles than from other silica particles. Furthermore, van der Waals attraction is dependent on the Hamaker constant, which is greater for particles with higher density¹. This means that the silica particles will possess stronger van der Waals attraction between each other than the latex particles will.

The combination of these two interactions means that the silica particles have an energetic preference to be in the vicinity of their own kind. This causes the silica particles to build up in areas inhabited by other silica particles resulting in the grid-like superstructures shown in Figure 1(a) and (d). In films with higher silica volume fractions, the particles spread further, starting to cover the latex particles and create structures that are more heterogeneous, with less cavities. This can be seen in Figure 2, where there are regions in which the silica has started to build up from the grid-like structure.

Increasing the evaporation rate has two effects on the structures. Firstly, the latex appears to be much more disordered, as the holes in the silica structure are widely spread and have no long-range ordering. Secondly, as described earlier, the fast evaporation rates enhance diffusiophoresis and result in a much greater concentration of silica particles at the surface.

Figure 7. Images taken from Brownian dynamics simulations of the binary blends before and after drying at (a-b) slow evaporation rates and (c-d) fast evaporation rates. The scale bars indicate the relative heights of the particles, measured in units of $R = D/2$ (the radius of the large particles).

Figure 7 shows the images obtained from the Brownian dynamics simulations that were carried out to model this system. Snapshots were taken before and after the upper wall descends. As seen in Figure 7(b), the small particles position themselves within the voids between larger particles. As the small particles feel less of a repulsion between themselves than with the larger particles, they build up from the voids rather than covering the larger particles. The resulting structure is a grid-like superstructure, extending slightly above the height of the large particles. These results

are very similar to the experimental results observed when drying films at slow evaporation rates (Figure 1 (a) and (d)).

When simulating the conditions for faster evaporation rates the small particles do not pack as neatly. They still do not cover the large particles closest to the surface, resulting in some holes. However, large particles at lower heights are now covered, creating a surface with much higher coverage of smaller particles and less holes. Unsurprisingly, the structures are also much more heterogeneous. Again, these results match those found experimentally at high evaporation rates (Figure 1 (c) and (f)).

Application as Abrasion Resistant Coatings. Silica nanoparticles do not deform during the latex film formation process, as they are hard particles. This means that surfaces consisting of only silica particles are unlikely to be stable and will therefore display poor abrasion resistance. Figure 8(d) shows an AFM image of a binary latex/silica film (dried at room temperature, with $\phi_{Si} = 0.17$) following abrasion testing with a felt pad using a force of 2 N for 100 cycles at a rate of 50 cycles per minute. The image clearly shows that a substantial amount of silica was removed as the latex structure can be seen at the top surface.

To overcome this weakness, we produce ternary colloidal films containing additional small latex particles (average diameter ~ 55 nm). The aim is that the small latex particles undergo the same size segregation as the silica nanoparticles, resulting in a film surface containing both of these smaller particles. The small latex particles deform during drying to enhance the surface stability of the film, while the silica particles provide enhanced mechanical properties. We also consider the effects of annealing these films to enhance interdiffusion and further improve the stability of the surface. For this study a volume ratio of 15:15:70 (between silica, small latex, and large latex) was chosen. This volume ratio was used such that the silica concentration was

similar to that of binary films with $\phi_{Si} = 0.17$, and the overall ratio between larger and smaller particles was similar to that in binary films with $\phi_{Si} = 0.29$.

Before producing ternary films, we dried blends containing only the two latex particles to investigate the segregation effects between them. Figure S4 in the SI shows that the small latex particles self-assemble at the surface, in the same way as the silica particles. The surface structures are also similar, with the small latex particles forming superstructures templated by the larger latex below. Figure 8(b) shows the AFM topography image of the ternary films. The structures formed are very similar to those in the binary films. The coverage of small particles appears to be slightly reduced, and the superstructure is more heterogeneous. It is likely that this is caused by the difference in particle size between the silica and small latex particles, as well as a larger polydispersity of the silica particles, leading to a reduced packing efficiency. The zeta potential of the small latex particles was measured at -25.2 mV. It is therefore highly likely that the superstructures observed in ternary films are formed by the same mechanisms as the binary films, with the smaller particles having a stronger repulsive interaction from the large latex particles than with each other or the silica particles. Annealed ternary films were also prepared (Figure 8(c)) to investigate the effect of latex particle coalescence and interdiffusion on the abrasion resistance.

AFM topography images of the ternary films following abrasion tests are shown in Figure 8(e-f). The images show that the surface structures are largely unchanged by the abrasion test. The same grid-like superstructures can still be seen. To quantify the surface stability and abrasion resistance of the films, EDX was carried out before and after abrasion testing. As shown in Figure 9, the concentration of silicon at the surface of binary films decreases by nearly 50 % after the abrasion test. It is clear from this result, and the AFM images shown in Figure 8, that a

large quantity of silica particles are being removed from the surface. The concentration of silicon at the surface of ternary and annealed ternary samples is lower than for the binary sample prior to abrasion testing. Given that the ternary films have small latex particles at the surface in addition to the silica, it is to be expected that the silicon concentration (by wt%) will be lower. More important is the difference in silicon concentration at the film surface before and after abrasion testing. For the ternary films there is little to no difference. Clearly, these films have a much more stable surface, and have enhanced abrasion resistance compared to the binary films.

Vickers hardness tests were carried out to assess the effect that silica nanoparticles have on the mechanical properties of the latex films. Hardness measurements for the binary films dried at different evaporation rates can be seen in the SI in Figure S5. The results show that there is a positive correlation between silica content and hardness, with increases of up to 7 HV_{0.01}, compared with films containing only latex. However, no clear relationship is observed between the hardness and the silica concentration at the film surface. We therefore conclude that the hardness values are affected by subsurface silica that is not detected by EDX. To provide evidence for this theory, we compare the penetration depth of the EDX analysis and the indentation depth of the hardness tests.

Figure 8. AFM topographic images of binary, ternary, and annealed ternary films (a-c) (dried at moderate evaporation rates) before and (d-f) after abrasion tests using a force of 2 N for 100 cycles, at a rate of 50 cycles per minute. All image sizes are 3 x 3 μm .

The indentation depth for Vickers hardness tests can be estimated as $t = d/7$, where d is equal to the diagonal length of the indentation⁵⁵. It was calculated that the indentation depths for all films were between 7 – 20 % of the total film height. These indentation depths are much greater than the heights of the silica superstructures at the film surface, indicating that subsurface silica particles will have an effect on the hardness measurements. Also, all samples having indentation depths of less than 20 % indicates that there are no substrate effects on the hardness measurements.

The penetration depth of the electron beam used for EDX analysis can be estimated using the Kanaya-Okayama formula:^{56,57}

$$R = \frac{0.0276AE_0^{1.67}}{Z^{0.89}\rho},$$

Where A is atomic weight, E_0 is beam energy, Z is atomic number, and ρ is density. For silicon, the penetration depth of EDX analysis (with an acceleration voltage of 5kV) is 589 nm. This equates to less than 1 % of the total film height. These two calculations show that the hardness measurements can be affected by subsurface silica nanoparticles which are not detected by the EDX analysis.

Figure 10 shows the results from hardness tests completed for binary, ternary, and annealed ternary films, before and after abrasion. These results are compared to a control latex film containing only the large latex particles. It was calculated that the indentation depth for all films was below 10% of the total film height meaning that there was no substrate effect and the results were reliable. It can be seen in Figure 10, that the introduction of silica to the latex film increases the Vickers hardness from 0.64 to 2.85 HV_{0.01}, an increase of over 400 %. This hardness is maintained in the ternary films, despite the presence of more latex particles at the topmost surface, and by annealing the films, the hardness is improved further, to 4.5 HV_{0.01}. This is likely a result of enhanced chain interdiffusion between latex particles at raised temperatures leading to stronger particle interfaces.

Figure 9. Graph showing the concentration of silicon (calculated by EDX) at the surface of binary (B), ternary (T), and annealed ternary (TA) films (dried at moderate evaporation rates) before and after abrasion (Abr.) testing.

Figure 10. Graph of the Vickers hardness of the binary (B), ternary (T), and annealed ternary (TA) films (dried at moderate evaporation rates) before and after abrasion (Abr.) testing. The hardness of the control latex is also shown.

Following abrasion, the hardness of the binary sample decreases slightly, but still remains much higher than for the control latex sample. It is therefore likely that there are silica nanoparticles dispersed below the topmost surface, within the top 10% of the film height. The hardness of the annealed ternary sample remains unchanged, which is to be expected because the abrasion test had little effect on the film surface. Meanwhile, the hardness of the ternary film after abrading actually increased slightly. However, this may just be a slight difference between two ternary samples. The same sample could not be used for both hardness tests since the second set of indentations may be affected by the first.

CONCLUSIONS

We have demonstrated a single-step, environmentally friendly, production method for latex composite films with improved hardness and abrasion resistance. We have reported the conditions under which binary latex/silica films undergo self-assembly, resulting in film surfaces enriched with silica nanoparticles. Furthermore, we show that the surface morphology and silica coverage can be controlled by the silica volume fraction and evaporation rate. Increasing either of these variables tends to increase the silica coverage and the height of the silica superstructures. Greater evaporation rates enhance the diffusiophoresis effect, increasing the concentration of silica particles at the surface of the drying film. In addition, heating the substrate can produce thermal Marangoni flows, forcing more silica particles to the surface. One method to investigate the separate effects of evaporation rate and thermal Marangoni flows would be to control the evaporation rate by tuning the humidity rather than heating the substrate.

We have explained the grid-like morphologies of the silica superstructures by considering van der Waals forces and electrostatic interactions between particles during drying. We suggest that relatively large repulsions between latex and silica particles cause the silica to build up in the

voids within the hexagonally packed latex structure. Higher evaporation rates alter the homogeneity of the latex structures, leading to less ordered superstructures with greater coverage. We have provided insights on the late drying stages through Brownian dynamics simulations of the drying of particle blends which agree with the experimental results. To provide further evidence for this theory the surface charge of the particles could be altered using surfactants. Utilising cationic surfactants should reduce the repulsion forces between latex and silica particles suppressing the formation of grid-like superstructures. In addition, it would be beneficial to carry out in-situ experiments to unravel the evolution of structures at the film surface.

We have reported experimentally, for the first time, the size segregation during drying of ternary latex blends. AFM imaging following abrasion tests highlighted the poor surface stability of binary latex/silica blends, showing that the silica superstructures were being wiped off the surface. We improved the stability by utilising ternary dispersions containing additional small latex particles. When drying these latex blends the film surface becomes enriched by both silica and latex particles. The latex particles undergo deformation, improving the stability of the film surface. AFM imaging and EDX show that the silica concentration at the surface was maintained following abrasion tests. In addition, the film hardness and superstructure morphologies of the ternary films are maintained. The hardness was improved further by annealing these films.

In this work we go one step further towards harnessing colloidal self-assembly for practical coating applications, by expanding the range to ternary films and providing insights on the formation of colloidal superstructures. The self-assembly of small latex particles within ternary colloidal systems could be utilised to enhance the properties of many systems that have recently been studied, making them more applicable to industrial use by improving their surface stability

and abrasion resistance. Furthermore, colloidal stratification can be controlled with greater ease by understanding the formation mechanisms behind the self-assembly of colloidal systems. Overall, the production methods used here will aid in the future development of more durable functional coatings using greener waterborne dispersions.

ASSOCIATED CONTENT

Supporting Information. Mixing ratios for colloidal films, dynamic light scattering data for all colloidal particles, measurements of hot plate temperature during film drying, elastic modulus maps, Péclet number calculations, ZJD state diagram, AFM image of binary latex-latex film, Vickers hardness measurements for binary latex/silica films. The supporting information is available free of charge at <http://pubs.acs.org>.

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