Use of a Routh-Russel Deformation Map to Achieve Film Formation of a Latex with a High Glass Transition Temperature

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ABSTRACT

In the film formation of latex, particle deformation can occur by processes of wet sintering, dry sintering, or capillary action. When latex films dry non-uniformly and when particles deform and coalesce while the film is still wet, a detrimental skin layer will develop at the film surface. In their process model, Routh and Russel proposed that the operative particle deformation mechanism can be determined by the values of control parameters on a deformation map. Here,

the film formation processes of three methyl methacrylate/butyl acrylate copolymer latexes with high glass transition temperatures (T_g), ranging from 45 to 64 °C, have been studied when heated by infrared radiation. Adjusting the IR power density enables the film temperature, polymer viscosity and evaporation rate during latex film formation to be controlled precisely. Different polymer particle deformation mechanisms have been demonstrated for the *same* latex under a variety of film formation process conditions. When the temperature is too high, a skin layer develops. On the other hand, when the temperature is too low, particles deform by dry sintering, and the process requires extended time periods. The deduced mechanisms can be interpreted and explained by the Routh-Russel deformation maps. Film formation of hard (high T_g) coatings is achieved without using coalescing aids that emit volatile organic compounds (VOCs), which is a significant technical achievement.

INTRODUCTION

The transformation of a waterborne polymeric dispersion into a cohesive polymer film is known as the latex film formation process. It is comprised of sequential, overlapping processes of water evaporation with particle packing, particle deformation, and diffusion of molecules to erase particle boundaries (1). The particle deformation mechanism plays an important role in defining the final film microstructure and properties, including permeability and tensile strength. Hence, this fundamental topic of colloid science has tremendous practical relevance.

Polymer particles can be deformed from their initial spherical shape into a polyhedral, space-filling structure via one of several mechanisms, including wet sintering, dry sintering and capillary deformation, depending on the process variables that determine whether the particles are deformed in the presence or absence of water (1-3). Wet sintering occurs when the time for

particle deformation is shorter than the time for evaporation to reduce the water level in the vertical direction. The wet particles are deformed in order to reduce the polymer/water interfacial energy. This mechanism was first proposed by Vanderhoff *et al.* (4) and experimental evidence has been presented by several authors (5-8). On the contrary, dry sintering occurs when particles are deformed in the absence of water, driven by the reduction in the polymer/air interfacial energy. In this case, the time needed for the particles to deform is longer than the evaporation time of water. This mechanism was originally proposed by Dillon *et al.* (9), and later Sperry *et al.* (10) presented experimental evidence for its occurrence. Finally, the condition for capillary deformation to occur is that the compressive capillary pressure (arising from the water meniscus between particles at the film surface (11)) is greater than the stress required to deform the particle network. Capillary forces have been calculated to be on the order of 10^{-7} N in a typical latex film (12), and have been measured experimentally (13). In the case of capillary deformation, water evaporation occurs simultaneously with particle deformation (5, 13). The two times are equal. There also is an intermediate regime in which the initial deformation of the particles occurs under capillary forces, but the final compaction of the film occurs by a dry sintering mechanism and only after the completion of water evaporation (6). This mechanism of a “receding water front” has been observed in experiments using cryogenic electron microscopy (3).

These various mechanisms of particle deformation were proposed and developed independently by the research teams outlined above. There was debate and confusion about which mechanisms are operative for a particular latex film. Much-needed clarity was offered when Routh and Russel (14-16) unified the mechanisms in their single process model, which considers the key process parameters. They placed each deformation regime in the parameter

space where they are operative, thus creating a so-called deformation map (see Figure 1a) that is used to identify the dominant mechanism for a particular latex and processing conditions.

Figure 1. (a) Routh-Russel deformation map for latex film formation. Reproduced with permission from Routh, A. F.; Russel, W. B., *Ind. Eng. Chem. Res.* 2001, 40, 4302-4308. Copyright (2001) American Chemical Society. (b) Illustration of skin formation when packed particles near a film surface are soft enough to deform and coalesce in the presence of water.

Deformation maps may be used to investigate how changing a parameter, such as the evaporation rate $\dot{E}$, the initial film thickness H , or the particle size R_0 , will influence the particle deformation mechanism. As can be observed in Figure 1a, deformation maps are dependent on two dimensionless control parameters, which are $\bar{\lambda}$ and the Peclet number (Pe). The parameter $\bar{\lambda}$ is defined as the ratio between the time needed for film compaction (that is, for complete particle deformation, t_{def}) and the characteristic time for the evaporation of water, t_{evap} . In this description, $\dot{E}$ is expressed as a velocity corresponding to the rate at which the water level falls as a result of evaporation. Then the control parameter is written as

$$\bar{\lambda} = \frac{t_{def}}{t_{evap}} = \frac{\eta_0 R_0 / \gamma_{wa}}{H / \dot{E}} = \frac{\eta_0 R_0 \dot{E}}{\gamma_{wa} H}, \quad (1)$$

where η_0 is the low shear viscosity of the polymer, and γ_{wa} is water-air surface tension. A high $\bar{\lambda}$ value means that the time required for particle deformation is longer than the evaporation time of water, such that the particle deformation will occur mainly when the water is gone, by a dry sintering mechanism. On the other hand, $\bar{\lambda}$ will be low when the time needed for water to evaporate is longer than the deformation time, and particles in water will deform by wet sintering. The parameter that has the strongest influence on the value of $\bar{\lambda}$ is the polymer viscosity, which is a strong function of the temperature of the process.

During film formation, the vertical inhomogeneity in the particle distribution also needs to be taken into account, as was considered by Sheetz (5). The vertical distribution (normal to the substrate) is determined by the balance between the evaporation of water, which leads to particle accumulation at the top of the film as the water level drops, and particle diffusion that will distribute the particles evenly in the vertical direction. The competition is described by Pe (Equation 2), which is the ratio between the characteristic time for the diffusion of the polymer particles from the top to bottom of the film, t_{diff} , and the evaporation time, t_{evap} . Using the Stokes-Einstein relation for the diffusion coefficient, D_0 , for a spherical particle in fluid with a viscosity of μ , Pe is defined as (1):

$$Pe = \frac{t_{diff}}{t_{evap}} \sim \frac{H^2 / D_0}{H / \dot{E}} = \frac{H \dot{E}}{D_0} = \frac{6\pi\mu R_0 H \dot{E}}{kT} \quad (2)$$

where k is the Boltzmann constant and T is the temperature of the film formation process. When $Pe \ll 1$, the diffusion of particles is relatively fast, so that as the water evaporates, the particles redistribute themselves to avoid being captured at the wet film surface. A homogeneous

distribution of particles in the vertical direction results. Slow evaporation rates, thin films and small particles all favor the homogeneous distribution of particles during latex film drying. When $Pe \gg 1$, the diffusion of the particles is slow, and they tend to accumulate at the top of the film. Cryogenic electron microscopy has been used to visualize a packed particle layer at the top of drying latex films.(17) Measurements of the water concentration gradients in the vertical direction during film formation are in agreement with the predictions of the Peclet number (18). Chen *et al.* (19) characterized the first three stages of film formation at different temperatures and relative humidities. They showed that Pe decreased with decreasing temperature and increasing relative humidity. The effect of sedimentation during latex film drying has also been considered in a recent model, in combination with the effects of evaporation and diffusion. Cardinal *et al.* mapped out the regimes where each process is dominant.(20) They found good agreement between the model predictions and particle concentration profiles found with cryogenic electron microscopy analysis. In the present work, only the Peclet number will be considered. Our latex particles are small (radius of about 75 nm) and have a density close to the continuous water phase (1 g cm^{-3}), so sedimentation effects are negligible.

In the high Pe regime, if the value of $\bar{\lambda}$ is low (<10), then the packed particles near the top of a film will deform and coalesce in the presence of water, via a wet sintering mechanism. A dilute dispersion will exist below the compacted surface layer. When these packed particles coalesce into a continuous film, it is called a skin layer. Transport of water through the polymer phase is slower than through the void space between particles. Hence, a skin layer is implicated in the entrapment of water in drying films (1). Figure 1a shows the region on the deformation map where skin formation is expected, and the process of skin formation is illustrated in Figure 1b.

In 1981, Okubo *et al.* described a “porous skin above a wet layer of flocculated particles” in their study of latex film formation.(21) Since that time, there have been numerous reports of the development of skin layers during latex film formation (22-25), but the results have not yet been fully interpreted in terms of the original Routh-Russel model. In most applications, there is a desire to avoid skin formation. The process model predicts that skin formation can be avoided with conditions that have a sufficiently high $\bar{\lambda}$ and a low Pe . When $\bar{\lambda}$ is too large, however, there is particle deformation by dry sintering, and interparticle voids can persist in the film for long periods of time. This trade-off is considered in the present work.

Routh and Russel (15) interpreted previously published reports of deformation mechanisms in the literature in the context of their process model. Since then, the model has been extended to include a constitutive relation on the basis of Hertzian contacts between particles (26), and there have been experimental studies of stress development during film formation (2, 13). Yet, over the decade since the Routh-Russel model was first developed, a comprehensive experimental test of the model has been lacking. In particular, there has been no convincing evidence that adjusting the process parameters ($\bar{\lambda}$ and Pe) on the Routh-Russel deformation map can lead to a single latex formulation undergoing all of the various mechanisms of particle deformation. Such a study requires a precise control of T , $\dot{E}$ and η_0 .

Recently, Georgiadis *et al.* (27) reported a new processing method to achieve the film formation of latex particles that are in a glassy state at room temperature. A hard film was formed without the introduction of coalescing aids (28-30). Their process uses near-infrared IR) radiation to heat the film above the glass transition temperature, T_g , of the polymer. They achieved film formation of an acrylate polymer with a T_g of 38 °C via a process they called infrared radiation-assisted sintering (IRAS). The use of radiative heating provides unprecedented

control over the temperature of a latex film through the power density of the IR source and the distance between the source and the film (31).

The objective of this work is to use radiative heating to adjust the process parameters ($\bar{\lambda}$ and Pe) to achieve film formation in different regimes of the deformation map of Routh and Russel. IR heating offers the distinct advantage of being able to tune the temperature, and hence the evaporation rate and polymer viscosity, over a wide range of values. It is shown that a single latex can form a film by several different mechanisms. These experiments constitute the first major experimental test of the Routh-Russel process model of latex film formation. The T_g of the polymer provides a convenient parameter that can be used to adjust the polymer viscosity at a particular temperature, as a means to map out different deformation regimes. Here, three different “hard” acrylate latexes, with T_g values of 45 °C, 55 °C and 64 °C, are used, and the deformation mechanism is deduced from the final film characteristics. The best experimental conditions in order to produce a hard film with good quality are defined.

MATERIALS AND METHODS

Materials

Methyl methacrylate (MMA) and butyl acrylate (BA) monomers were used as received from Quimidroga (Spain) without further purification. Sodium lauryl sulphate (SLS, Aldrich) was used as an emulsifier and 4, 4'-azobis (4-cyanovaleric acid) (V-501, Fluka) as an initiator. Sodium hydroxide (NaOH, Panreac) was used to dissolve the initiator in water. Doubly deionized (DDI) water was used throughout the work.

Synthesis of MMA/BA latexes by emulsion polymerization

Three different copolymers of MMA/BA (65/35, 70/30 and 75/25 wt.%) were synthesized by seeded semicontinuous emulsion polymerization. Initially, a seed composed of a MMA/BA copolymer (65/35, 70/30 or 75/25 wt.%) at 20 wt.% solids content was prepared with SLS (1 % by weight based on monomers, wbm) and V-501 (1 % wbm) in a 1000 mL glass jacketed reactor equipped with a reflux condenser, a N₂ inlet, a sampling device, a stainless steel modified anchor stirrer rotating at 250 rpm and a cascade temperature control system (Camile TG, Biotage). After one hour of batch reaction, the seed was formed and the semicontinuous polymerization was started using the same reactor setup. First of all, the initiator (V-501, 1 % wbm), dissolved in water (6 wt %, adding a stoichiometric amount of NaOH), was introduced in a shot and then the rest of the ingredients were fed in one stream containing the pre-emulsion of MMA and BA (59 % S.C. and SLS 1 % wbm) to achieve a final weight solids fraction of $\phi = 0.4$. After the feeding period (3 h), the system was allowed to react in batch for one more hour. Total conversion was achieved in all the cases (as measured by gravimetry). The average particle diameters were around 150 nm in all the cases, determined by dynamic light scattering, using a Malvern Nanosizer. The T_g values of the dry copolymers, measured by differential scanning calorimetry (Q2000, TA instruments) at a heating rate of 10 °C/min, were 45 °C, 55 °C and 64 °C for the 65/35, 70/30 and 75/25 copolymers, respectively.

IRAS experiments

Latex films were directly cast onto clean, glass substrates from a micropipette and spread uniformly. The initial thickness of the wet film, H , was adjusted by depositing the required mass of the wet latex across a known area. A 4 kW carbon IR emitter (Heraeus Noblelight) of 0.7 m

length and a maximum power of 150 kW/m^2 was used to heat the films. At this maximum power, the emitter has a temperature of 1200°C , which corresponds to a peak emission wavelength of $2 \mu\text{m}$. This type of emitter has a very fast response time such that it reaches its maximum temperature within 1-2 s. The emitter was placed at a distance of 20 cm above the wet latex film. Coatings were made using different initial film thicknesses and with the power of the emitter, P_E , ranging from 800 to 2400 W. The power density from the carbon IR emitter was measured using an optical power meter (Anritsu, ML910B) with a sensor range between $0.75 \mu\text{m}$ and $1.8 \mu\text{m}$ (Anritsu, MA9711A). The temperature of the film during the IRAS processing was recorded using a digital thermocouple wire attached to the substrate and in contact with the wet latex film. Evaporation rates of the water during IRAS film formation experiments were recorded by placing the wet film on an electronic balance (Sartorius Extend ED2202S-CW) interfaced with a computer to record the data. The balance was shielded from the intense IR radiation by placing insulation on the sample pan. Figure 2 (a) shows the experimental set-up.

RESULTS AND DISCUSSION

Figure 2 (b) shows the evolution of the temperature and the loss of mass in the film as a function of time in a typical IRAS experiment. As can be observed, the mass of the film decreased at a constant rate, until nearly all the water was evaporated and the mass approached a constant value. This point (the point at which the rate of mass loss reached zero) is defined as the experimental drying time (t_{dry}). This parameter is very important from a practical point of view, as it can be used to estimate how long is needed for a coating to be exposed to the infrared radiation in order to remove all the water (31). Furthermore, Figure 2 (b) shows how the water loss rate is estimated from the slope, S , of the mass-time data in units of g/s. Then $\dot{E}$

(representing the velocity at which the surface recedes) is calculated by assuming a density of water of $\rho = 1 \text{ g cm}^{-3}$, and using the measured area, A , of the coating (cm^2) from $S/\rho A$.

Figure 2. (a) Experimental set-up for simultaneous measurements of temperature and mass of a latex film under IR radiation. (b) Simultaneous evolution of the temperature and the mass of the wet latex film in a typical IRAS experiment. The experiment was performed using the latex with a T_g of 55 °C and a film with an initial thickness of $H = 0.5 \text{ mm}$. The power of the IR emitter was 1200 W, which leads to a power density of 25 mW cm^{-2} at a distance of 20 cm. The dashed line shows the best fit line used to calculate $\dot{E}$ for this experiment, and t_{dry} is identified from the time when all of the water mass is lost and the mass is constant.

Observing the evolution of the temperature over time in Figure 2 (b), two different stages can be distinguished. At the beginning of the experiment, there is a sharp increase in the temperature, but after *ca.* five minutes it approaches a plateau. At *ca.* 15 min. of radiation, a second plateau is reached after a second pronounced increase in temperature. Intriguingly, t_{dry} is observed near the time of the second increase in the temperature. The first plateau can be explained through a steady state in which the thermal radiation supplies the heat of vaporization for water ($Q = 2.3$

kJ/g) (32) required to evaporate the water. Hence, the absorbed heat does not lead to a rise in the temperature. Then, when the water has been removed at a time of t_{dry} , the absorbed heat raises the temperature of the polymer sharply, because it is no longer supplying the heat of vaporization. The heat required to evaporate the water from a wet film of thickness H and a solids content, ϕ is calculated at $QH(1-\phi)\rho$. Using typical values of $H = 250$ mm and $\phi = 0.4$, then the required heat is 34 J cm^{-2} .

The measured power densities from the lamp range from 6.7 mW cm^{-2} to 52 mW cm^{-2} (as the IR emitter power is varied between 800 and 1600 W). At the maximum power density, enough energy is supplied to the film in about 10 minutes to evaporate all of the water, provided that all of the radiation is absorbed. (In reality, not all of the radiation is absorbed. However, heat is also supplied by the substrate and the surrounding atmosphere.)

In all of the experiments, a general trend was observed when films with the same initial wet film thickness are compared. When the power of the IR emitter is higher, the rate of temperature increase is greater. Consequently, the evaporation rate increases and the drying time decreases. An example for the latex with a T_g of 45°C is shown in Figure 3 (a), where the temperature and mass of the film are plotted against the time of IR irradiation. At all powers of the IR emitter, a plateau in the temperature is observed, but it increases in length as the power increases. The measured evaporation rates likewise increase in proportion to the power of the IR emitter, and the time to dry decreases (Figure 3 (b)). These results are in agreement with those reported by Georgiadis *et al.* (31), who likewise found that the evaporation rate has a linear dependence on the radiation's power density, whereas the drying time is inversely proportional. Furthermore, these evaporation rate values, ranging between 3 and $8 \times 10^{-5} \text{ cms}^{-1}$, are on the same order of magnitude measured by Rösler and co-workers (33) for water evaporation under IR radiation.

They showed that evaporation rate of water in waterborne coatings is faster when IR radiation heating is used instead of heating by convection.

Figure 3. (a) Evolution of the temperature over time when using the IR emitter at different values of power, P_E . (b) Evaporation rates (■) and drying times (●) as a function of the IR power density. Experiments were performed on a latex with a T_g of 45 °C and initial film thickness of $H = 0.5$ mm.

One of the main objectives of this research is to generate experimental evidence for the deformation maps. Therefore, film formation was carried out with a range of film thicknesses, H , and IR power density settings, as are listed in Table 1. Then $\bar{\lambda}$ and Pe pairs were calculated for each different experiment using Equations 1 and 2, respectively. The original particle radius (R_o) is a known parameter. The viscosity of the water (μ) (34) and the water-air surface tension (γ_{wa}) are both dependent on the film formation temperature. The latter is also dependent on the surfactant concentration and hence could vary throughout the film formation process (1). Nevertheless, the standard values of $\mu = 1.00$ mPa s and $\gamma_{wa} = 72.8$ mN/m for water at room temperature were used in the calculations. Any error in γ_{wa} would affect the value of $\bar{\lambda}$ only

within a factor of two, whereas the control parameter spans several orders of magnitude in the experiments. The variable that has the strongest influence on $\bar{\lambda}$ is the low shear viscosity of the polymer (η_0). η_0 was estimated using a form of the Williams-Landel-Ferry (WLF) equation (36):

$$\eta_0 = 6.5 \cdot 10^{10} \exp \left[\frac{-34(T-T_g)}{80+T-T_g} \right]. \quad (3)$$

This equation shows how η_0 is strongly dependent on the temperature. In our experiments, temperature was not a constant parameter, but it increased during the irradiation (Figure 2). The deformation maps are designed to be used at a constant temperature, such as room temperature. In order to calculate a single $\bar{\lambda}$ for each experiment, it is necessary to establish a characteristic value for η_0 . Hence, the temperature reached at one-half of t_{dry} was selected to be the representative temperature in each experiment and thereafter used to obtain a characteristic η_0 for the calculation of $\bar{\lambda}$. Although this is a gross simplification, it was applied consistently to all experiments. Hence, any errors affect the different experiments in the same way and therefore do not affect the trends in the parameters.

Pe and $\bar{\lambda}$ pairs were calculated for each film formation experiment, using measured or calculated values of the variables. The Supporting Information shows the calculations. The pairs were then plotted on the map in Figure 4 for the latex with a T_g of 55 °C, where the letter by each data point is used to identify the processing variables in Table 1. A wide range of process control parameters, spanning several orders of magnitude, were obtained. Each process was evaluated to determine its most likely mechanism of particle deformation, as described hereafter.

Table 1. Conditions used for experiments performed using the latex with a T_g of 55 °C

Experiment Code	Power of the IR emitter (W)	Power density (mW cm^{-2})	Initial wet film thickness, H (μm)	Characteristic temperature ($^{\circ}\text{C}$)
A	1200	25 ± 4	500	54
B	800	6 ± 0.03		48
C	1200	25 ± 4	380	53
D	800	6 ± 0.03		45
E	2400	160 ± 7	250	68
F	1800	67 ± 6		59
G	1200	25 ± 4		51

Figure 4. Deformation map obtained for the latex with a T_g of 55 °C. Symbols represent each deformation mechanism: (○) Skin formation, (●) Capillary deformation, (▲) Receding water front, (■) Dry sintering and (□) Non film-forming. The experiment codes listed in Table 1 are used to identify each data point.

Skin Formation

The conditions for experiment E correspond to a high Pe and relatively low $\bar{\lambda}$ value, situated in the bottom-right side of the deformation map. In all experiments, Pe was greater than unity, which predicts that the water distribution will be non-uniform in the vertical direction during the drying process. Figure 5 (a) shows a photograph of the film obtained in Experiment E. The

formation of a skin layer at the top of the film can be clearly observed. There was sufficient mechanical integrity in the skin layer for it to be peeled off to reveal a wet colloidal film underneath it. The observed skin formation agrees with the position of experiment E on the deformation map obtained from the Routh-Russel process model (Figure 1a) that predicts (partial) skin formation when $\bar{\lambda} < 100$ and $Pe > 1$. The drying kinetics during experiment E are shown in Figure 5 (b). In the first five minutes, the water evaporates at a constant rate. Thereafter, there is a distinct slowing down. This is characteristic of the development of skin layer. The free evaporation of water is blocked by a continuous layer of coalesced, and the rate-limiting step is the transport of water through the skin layer. The slowing down of water loss differs markedly from the data trend shown in Figure 2 for a film without skin formation.

Evidence for some partial skin formation was also found in experiment A. In this case, the $\bar{\lambda}$ value is higher than where skin formation is predicted to occur by the model. However, in this experiment, Pe is especially high (*ca.* 68), which offers some explanation, as follows. Routh and Zimmerman (37) derived a scaling relationship for the water concentration gradient in the vertical direction, $d\phi/dz$. When $Pe > 1$, they predicted that $d\phi/dz$ scales with $Pe^{0.5}$. Thus, when Pe is higher, a steeper concentration gradient is expected, which means that there is a more sharply-defined boundary between the packed particles at the top of a film and a dilute dispersion near the bottom. This general trend has been shown elsewhere to hold experimentally (38). Hence, when a skin is formed at higher values of Pe , as in experiment A, the boundary between the packed particles at the surface and the fluid region is expected to be sharper, which would make it detectable in experiments, even if it is not coalesced via wet sintering. These experiments teach us that a higher IR emitter power, leading to fast evaporation rates and a low

polymer viscosity, favours non-uniform drying and the formation of a coalesced skin layer on the top of the film.

Figure 5. (a) Photograph from experiment E demonstrating that the skin can be peeled away to reveal that the film is still wet underneath. (b) Mass loss occurring over time in experiment E. In the first five minutes, evaporation occurs at a constant rate. Then, there is a slowing down of the rate of water loss, which is characteristic of skin formation.

Dry Sintering and Capillary Deformation

It is well documented that inter-particle voids in colloidal films scatter light and create opacity (39). When dry sintering is the dominant particle deformation mechanism, an increase in the optical transparency of a latex film is expected after all the water has been lost. Figure 6 (a) and

(b) show photographs of films obtained from experiment G after two different times: 15 min. and 20 min. It is very important to point out here that the t_{dry} of this experiment was 8 min. Thus, the films shown in Figures 6 (a) and (b) were being heated by the IR radiation when they were dry. The film heated for 15 minutes is opaque after all the water has been removed. Its opacity is attributed to incomplete particle sintering. With an additional five min. of heating, optical clarity is gained as sintering in air continues. It can be surmised that in the conditions of experiment G, the time needed for particle sintering is longer than t_{dry} of the film, and therefore particles are deformed by dry sintering.

In order to test this interpretation, AFM images of the surface of both films were captured (Figure 7). AFM images demonstrate that in the film heated for 15 min. (Figure 7(a) and (b)), particles are not deformed significantly (all of them retained their initial shape), whereas when the film was heated for 20 min., there is extensive deformation of the particles, and the loss of their individual identity can clearly be observed (Figure 7(c) and (d)). This observed particle deformation occurred after the film had dried. Hence, it is concluded that dry sintering occurred in this region of the deformation map for Experiment G.

By comparison, in experiment F, in which there is a lower $\bar{\lambda}$, films were optically transparent at times at, or shortly after, t_{dry} . This result indicates that particle deformation and film drying occur on similar time scales, which is consistent with a mechanism of capillary deformation.

Figure 6. Photographs of the films obtained with the same latex ($T_g = 55\text{ }^{\circ}\text{C}$) using different process parameters: Films obtained in experiment G but irradiated for (a) 15 min. and (b) 20 min. (both longer than the t_{dry} of the experiments). There is a blue panel behind the substrates.

Figure 7. AFM height images ($1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ area) of the surface of the film from experiment G exposed to IR radiation (a, b) for 15 minutes and (c, d) for 20 minutes. The images on the right-hand side are three-dimensional.

Comparing the experiments in which the same film thickness but different IR powers are being used (*e.g.* experiments G, F and E in Figure 4), it can be observed that as the power of the IR emitter decreases, the points are shifted to lower Pe and higher $\bar{\lambda}$ values. As the power of the IR emitter is decreased, the evaporation rate of water is also decreased, leading to a lower Pe value (see Equation 2). In the same way, as the power density of the emitter is decreased, the characteristic temperature of the process is also decreased, leading to polymer particles with a higher viscosity and as a consequence obtaining higher $\bar{\lambda}$ values. It was observed that when moving to lower Pe and higher $\bar{\lambda}$ values, films dried more uniformly and therefore their visual quality improved.

Moreover, comparing the experiments with different initial wet film thicknesses but where the same emitter power was used (A, C and G), it was observed that as the thickness of the film was decreased, experiments were shifted to lower Pe numbers and slightly higher $\bar{\lambda}$ values, and again the quality of the film formed was improved when moving in that direction.

Film Cracking

In experiments where the IR emitter power was 800 W (Experiments D and B), severely cracked and opaque films were obtained (Figure 8). In these experiments the power density of the emitter was so low that the temperature during the experiment was not high enough to decrease the viscosity of the polymer sufficiently to enable the particle deformation. Cracking is attributed to the development of capillary stresses for which the total recovery of elastic energy counter-balances the additional energy of the polymer-air surface created in the crack. Russel *et al.* (26) determined the minimum capillary pressure, P_{cap}^{crack} , to open a crack as:

$$-\frac{HP_{cap}^{crack}}{\gamma} \cong 2.06 \left(\frac{\bar{G}H}{\gamma} \right)^{2/5} + \frac{2.91}{\tau}, \quad (4)$$

where $\bar{G}$ is an effective shear modulus for the packed particles with Hertzian contacts and τ is the relaxation time that is proportional to η_0 . The equation shows that decreasing polymer viscosity, as well as the initial film thickness, will suppress cracking in a latex film by increasing the capillary pressure required for crack propagation. With this in mind, an additional situation can be added to the deformation maps to account for film cracking at high $\bar{\lambda}$ values, where the temperature reached is not high enough to reduce the polymer viscosity to enable particle sintering in the dry state. The boundary between the dry sintering region of the deformation map and the cracked region is defined by the minimum film formation temperature, below which cracking will occur. Crack formation is known to be related to the process conditions. Specifically, the process conditions affect the evaporation rate, which in turn defines the point in time where the stress will be at a maximum, and the value of this maximum stress is proportional to the temperature-dependent polymer viscosity (13, 40). In previous work,(3,41) it has been demonstrated that crack spacing increases in proportion to the process temperature, and the onset temperature of film cracking can be used to deduce the polymer glass transition temperature (42).

Figure 8. Severely-cracked and opaque film obtained in the non film-forming region of the deformation map.

Significance of the Plateau Temperatures

Our results show that locating the process control parameters on a deformation map is a good indicator of the deformation mechanism. Additionally, we have discovered that the temperature reached in the first plateau is an important indicator of the particle deformation mechanism. The plateau occurs over times prior to t_{dry} , and so it represents the film in the wet state. Figure 9 shows the evolution of the temperature over time in experiments E, G and D, carried out with the latex with a T_g of 55 °C. In experiment D, the temperature of the plateau is approximately 45 °C, which is lower than the T_g of the polymer, and in this case a cracked film is obtained. In Experiment G, in which the temperature in the plateau (54 °C) is near the T_g of the polymer, a good quality film was obtained by a dry sintering deformation mechanism. Finally, in Experiment E, where the temperature in the short plateau (around 100 °C) is well above the T_g of the polymer, there was skin formation. Hence, the temperature reached in the experiment before all the water has been lost is a key parameter in determining the particle formation mechanism.

Figure 9. Evolution of the temperature for experiments D, G and E carried out with the latex with a T_g of 55 °C.

Practical Implications

As a general conclusion regarding the deformation map in Figure 4, it can be said that although not all the values fitted exactly to the model developed by Routh and Russel, similar trends were observed. Skin formation was observed when high temperatures and thick films were used. As the IR emitter power was decreased (leading to lower temperatures and lower evaporation rates of the water), the control parameters were shifted to the dry sintering region of the map. In our experiments, T was not constant, and hence a single value of η_0 could not be defined. Furthermore, η_0 was only estimated from the WLF equation. Hence, an exact agreement of numerical values between the experiment and model cannot be expected. Nevertheless, the deformation map is an excellent guide for achieving film formation in a hard latex, which is otherwise exceedingly difficult to achieve.

Figure 10 presents a deformation map in which all the experiments carried out with the three different latexes are shown. A similar trend to the one observed in Figure 4 is seen. In experiments situated in the right bottom corner of the map (high Pe numbers and relatively low $\bar{\lambda}$ values), a skin layer was formed. On the other hand, at high $\bar{\lambda}$ values, films cracked. It was observed that good quality films were obtained in experiments situated in intermediate regions, with intermediate $\bar{\lambda}$ values and lower Pe . Here, good quality refers to films that are crack-free and optically transparent and smooth. Skin formation leads to film buckling and a decrease in the film smoothness. Table 2 summarizes the conditions used to obtain good quality films for the latexes with the different T_g values. This research provides a way to overcome the so-called “film formation dilemma” of choosing between a “soft” film that is a good film former and a “hard”

film that requires coalescing aids and emits unwanted volatile organic compounds (VOCs) during film formation. (1, 43)

Figure 10. Deformation map for all the experiments carried out for latexes with three different T_g values as indicated by the colours: Blue: 45 °C; Red: 55 °C; Green: 64 °C. Symbols represent each deformation mechanisms: (○) Skin formation, (●) Capillary deformation, (▲) Receding water front, (■) Dry sintering and (□) Non Film-Forming.

Table 2. Conditions necessary to create transparent, crack-free films with latexes of different T_g values

T_g of the latex (°C)	Power of the IR emitter (W)	Power Density (mW cm^{-2})	Initial wet film thickness (μm)
64	2400	160 ± 7	250
55	1800	67 ± 6	250
55	1200	25 ± 4	250
45	800	6 ± 0.03	500

As a general trend, Table 2 shows that for a higher T_g of the polymer, a higher IR emitter power is necessary to obtain a good quality film. The reason is that the quantity $T - T_g$ influences

the viscosity, which in turn determines the particle deformation mechanism. As the power density of the IR emitter was increased, the evaporation rate of water also increased. With a higher Pe , a steeper concentration gradient of polymer particles in the vertical direction is expected. Consequently, for latexes with T_g values of 55 °C and 64 °C, where a greater T is required, the initial film thickness, H , needs to be necessarily decreased. Then, $Pe = HE/D_0$ is kept low enough to avoid significant skin formation and to ensure acceptable film quality.

In our experiments, the polymer is hydrophobic and hence is not expected to adsorb very much water. In more hydrophilic polymers, absorbed water will reduce the glass transition temperature of the polymer, in a process called water plasticization. As the latex dries, the T_g of the polymer would then be expected to rise, thereby leading to a fall in the viscosity at a fixed temperature. The process model could be adapted to include a dependence of viscosity on time. Additionally, the model could be extended to consider particle flocculation, which could allow particle deformation to precede the packing of particles in a bed and which would reduce the particle diffusivity.

CONCLUSIONS

The Routh-Russel process model provides an excellent framework in which to select the process control parameters to achieve the desired mechanism of latex film formation. IR radiative heating provides control of the temperature and thereby enables the evaporation rate and polymer viscosity to be adjusted to move to different positions on the deformation map. The experimental conditions leading to skin formation, dry sintering, and film cracking are in qualitative agreement with the expectations of the process model. The experiments and the resulting deformation map point the direction toward the right parameters to produce high

quality films from a hard latex. To avoid skin formation, the film temperature, and hence the IR emitter power density, must not be too high. Using the process model as a guide, films of good quality were obtained here from hard latices with T_g values of 45, 55 and 64 °C. Notably, film formation was achieved without using coalescing aids that emit VOCs, which is an important technical achievement that is made possible through application of the model.

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Supporting Information Available: Data tables listing the parameters used in the calculation of $\bar{\lambda}$ and Pe for all experiments. This material is available free of charge via the Internet at <http://pubs.acs.org/>

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Table of contents only