

Buckling and Crumpling of Drying Droplets of Colloid–Polymer Suspensions

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Spray drying of complex liquids to form solid powders is important in many industrial applications. One of the challenges associated with spray drying is controlling the morphologies of the powders produced; this requires an understanding of how drying mechanics depend on the ingredients and conditions. We demonstrate that the morphology of powders produced by spray drying colloidal polystyrene (PS) suspensions can be significantly altered by changing the molecular weight of dissolved poly(ethylene oxide) (PEO). Samples containing high-molecular-weight PEO produce powders with more crumpled morphologies than those containing low-molecular-weight PEO. Observations of drying droplets suspended by a thin film of vapor suggest that this occurs because the samples with high-molecular-weight PEO buckle earlier in the drying process when the droplets are larger. Earlier buckling times are likely caused by the decreased stability, demonstrated by bulk rheology experiments, of PS particles in the presence of high-molecular-weight PEO at elevated temperatures. We present a consistent picture in which decreased particle stability hastens droplet buckling and leads to more crumpled powder morphologies; this underscores the importance of interparticle forces in determining the buckling of particle-laden droplets.

Introduction

As complex fluids dry from liquid to solid states, they manifest a variety of mechanical behaviors that are of both fundamental and practical interest. Spray drying is a common industrial process that involves the rapid drying of aerosols and is an important method of manufacturing large quantities of foodstuffs, pharmaceuticals, and detergents.^{1,2} In many spray-drying applications, it is critical to control the morphology of the powders produced because powder morphology can significantly affect manufacturing processes after spray drying, as well as the appearance of the final products.

A common morphology manifested by spray-dried materials is that of a buckled appearance. In some industrial applications, this morphology is undesirable. To prevent or control buckling in such applications, it is valuable to understand the physical origins of buckling. The buckling of shrinking droplets has been observed in other complex fluids, including particle-stabilized emulsion drops³ and sessile polymer drops.^{4–6} In spray drying, buckled morphologies are commonly seen in powders dried from suspensions of colloidal particles. Buckling can occur in these systems because the receding surface of the drying droplet gives rise to a particle-dense region at the surface of the droplet. As drying continues, the particles eventually pack closely enough that interparticle repulsions resist further shrinkage. The solvent, however, continues to vaporize through the interstices between

the particles. The decrease in solvent volume causes the fluid menisci between the closely packed particles to recede into the droplet. This causes the curvature of the menisci and the droplet pressure to decrease.^{3,7a,7b} The decrease in droplet pressure exerts a compressive capillary stress on the particle shell. When this stress becomes sufficiently large to overcome the repulsive forces between the particles, the outer shell undergoes a sol–gel transition.⁸ Further solvent loss causes the outer shell to buckle and crumple, leading to dried powders with buckled or wrinkled morphologies.

Interparticle forces play a critical role in determining when and if a droplet buckles; thus any ingredients that modify these forces may effect the buckling behavior of the drying droplet.⁸ Polymers are common ingredients in spray-drying mixes. Moreover, they can significantly alter the interactions between solid particles. It is therefore expected that the presence of polymers can significantly alter the buckling behavior of solid suspensions. The purpose of this article is to probe such effects. We studied an aqueous suspension of charge-stabilized polystyrene (PS) particles containing dissolved poly(ethylene oxide) (PEO). This is a useful model system because PS and PEO are common ingredients in industrial spray-drying applications and PEO can both stabilize or destabilize PS, depending on the molecular weight of the PEO and the temperature.^{9,10} We investigated how changing the molecular weight of PEO affects powder morphology, buckling, and particle–particle interactions. We studied powder morphology with scanning electron microscopy (SEM). Because direct visualization of buckling during spray drying is not practical, we observed the drying of single droplets suspended above a hot plate by a thin film of water vapor originating from each droplet, a condition we expect to mimic spray drying conditions. This allowed us to observe droplet

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buckling and other shape transitions with a high-speed camera. Finally, we studied particle–particle interactions by performing bulk rheology experiments.

From these experiments, a consistent picture of physical mechanisms occurring during the drying process emerges: when particles are less stable to aggregation, buckling occurs sooner and the particle morphology is more crumpled. Our results underscore the potential usefulness of the single-droplet experiments in studying spray drying. Single-droplet experiments are not only simpler to perform than spray-drying experiments but also require 10^{-4} of the material needed for a small spray-drying experiment.

In the final section of this article, we describe new droplet behavior, such as violent droplet explosions, observed during single-droplet experiments and discuss the insights that these events provide into the transient viscoelastic properties of the droplets during drying.

Experimental Details

Spray Drying. Spray-drying experiments were carried out with PS latex particles prepared by an emulsifier-free emulsion polymerization method.^{11–13} First, a 500 mL round-bottomed flask equipped with a stirrer, a condenser, a nitrogen inlet, and a thermometer was charged with deionized water (264 mL). The system was heated to 80 °C for about 30 min while bubbling with nitrogen gas to remove oxygen from the reactor. When the reaction temperature reached 80 °C, we added to the reactor an initiator solution that consisted of 0.15 g of $K_2S_2O_8$ in 10 mL of deionized water. Five minutes later, a mixture of styrene (15 g) and acrylic acid (0.75 g, neutralized with an appropriate amount of NaOH) was added to the reactor and allowed to polymerize for 6 h at 80 °C while being rotated in a heat bath at 200 rpm. The resultant particle radii were approximately 350 nm and were stabilized by charged groups on the particle surface. The concentration of acrylic acid was adjusted so that the surface charge was roughly similar to that of the commercial particles (Interfacial Dynamics Corporation, IDC) that were used for single-droplet experiments. To roughly compare the surface charges of the two particle types, we prepared solutions with equal volumes and similar volume fractions. We then centrifuged both samples simultaneously and compared the levels of sedimentation. Particles with more charge were less likely to aggregate and sediment than particles with less charge. The amounts of initiator and acrylic acid were adjusted until both types of particles produced roughly the same height of sediment.

Solutions used for spray drying were 250 mL in volume, containing 0.05 wt % PEO and 0.2 wt % PS. Four molecular weights of PEO were used; $M_w = 10^3$, 10^4 (both obtained from Fluka), 10^5 , and 10^6 (both obtained from Aldrich), where M_w is measured in g/mol. We used a spray dryer (LabPlant SD-06) equipped with a two-fluid nozzle for atomization. The inlet temperature was fixed at 200 °C, the outlet temperature was about 78–80 °C, and the feed rate of the suspension was 30 mL/min. Spray-dried PS and PEO powders were collected by means of a cyclone.

Analysis of the spray-dried powders was performed using a scanning electron microscope (SEM, LEO 982) operating at 2 kV with a filament current of approximately 0.5 mA. Powder samples were deposited onto SEM stubs covered with adhesive tape; they were then coated with a platinum–palladium layer using a Polaron SC7620 sputter coater operated for 120 s at a sputtering current of 40 mA.

Single-Droplet Experiments. Because it is difficult to observe individual droplets being spray dried, we attempted to mimic the conditions of spray drying in a system that allowed us to observe the drying of individual droplets easily with a high-speed camera. Single droplets were levitated above a hot stainless steel plate by

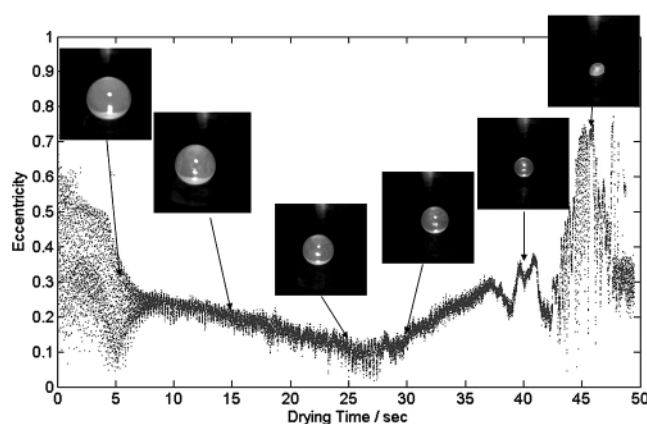


Figure 1. Representative plot showing how droplet eccentricities evolve during the drying of a single droplet containing only PS. Eccentricity measurements are noisy during the initial 8 s of the experiment because of initial droplet motion after deposition. Eventually, the droplet settles to the bottom of the concave surface, and the eccentricity gradually decreases because of the increased importance of surface tension relative to gravity as the droplet shrinks. The upturn in eccentricity occurring at about 27 s corresponds to the droplet shell becoming solidlike and defines the time of buckling, t_b .

a thin layer of their own vapor, an effect known as the Leidenfrost effect.¹⁴ This drying scheme is different from spray drying in many respects. For example, as a droplet moves through a spray drier the humidity and temperature of its environment can change dramatically. Spray drying is difficult to model because it is a complicated process with many possible configurations and variables. Nevertheless, we feel that the single-droplet experiments capture the basic physics of suspension droplets that rapidly dry while being suspended in air.

Single-droplet experiments were carried out using monodisperse PS particles of radii 110 and 1000 nm obtained from IDC. The particles were charge stabilized by carboxylate groups on the PS surface. Both PS and PEO were added in the same concentration by weight as in the solutions used in spray-drying experiments (PEO at 0.05 wt % and PS at 0.20 wt %). Because both the homemade and the IDC particles had roughly the same charge, both sets of particles are expected to behave similarly, despite their differences in size.

The hot plate used in the experiments was concave to prevent the droplet from escaping and was maintained at a temperature of 200 °C, the inlet air temperature used in the spray-drying experiments. A pipet was used to deposit 10 μ L droplets on the plate. Upon deposition, the droplets moved quite vigorously but eventually settled to the bottom of the concave plate where their drying was recorded by a high-speed camera (Phantom V9) at a rate of 500 images/s. The setup was illuminated by a halogen spot lamp.

Image analysis was performed on each video frame using the image processing toolbox of MATLAB 7.0 software. The shape of the white droplet against the dark background was determined by a binary sorting of pixels using a manually selected threshold. The software then fit the shape of each droplet to an ellipse having the same second moments as the droplet area. The eccentricity, e , of the fitted ellipses provides a measure of how spherical each droplet was; $e = 0$ corresponds to a spherical shape, and $e = 1$ corresponds to a line.

A representative evolution of e measured with respect to time, t , during a drying experiment on a drop containing 0.2 wt % PS (with radii of 110 nm) is shown in Figure 1. Eccentricity plots of droplets containing PEO as well as PS had similar features to the plot shown in Figure 1 but were noisier because of the droplet behavior described in the section Ripples, Explosions, and Jumps. In Figure 1, $t = 0$ s corresponds to the deposition of the droplet. From $t = 0$ to $t = 8$ s, the data is noisy because of the initial droplet motion caused

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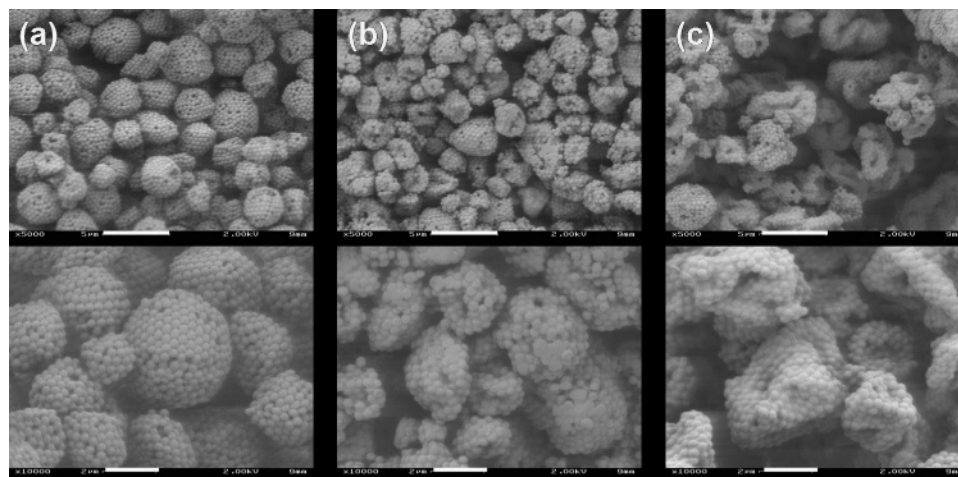


Figure 2. SEM images of spray-dried powders made from suspensions of PS and (a) no PEO, (b) low-molecular-weight PEO ($M_w = 10^4$), and (c) high-molecular-weight PEO ($M_w = 10^6$). The scale bars on the upper three images represent $5\ \mu\text{m}$ (lower magnification), and the scale bars on the lower three images represent $2\ \mu\text{m}$ (higher magnification). Increasing the molecular weight of PEO made the powder shape more crumpled.

by the deposition. Eventually the droplet stops moving, and the eccentricity steadily decreases until about $t = 27\ \text{s}$. Then the eccentricity steadily increases until about $t = 37\ \text{s}$, when the solidlike nonspherical pellet begins to rotate and maintains a pelletlike shape, suggesting solidlike characteristics. The rotations of the pellet cause the oscillations in eccentricity seen in Figure 1. From $t = 44\ \text{s}$ until the end of the experiment, the data becomes noisy again as the small aggregate rapidly bounces before eventually attaching to the hot plate and boiling away.

When the drops are liquid, their shapes can be interpreted as a balance between the effect of surface tension, γ , which favors spherical droplets, and gravity, which favors flat droplets. The force associated with the surface tension scales as γa , where a is the droplet radius. The force of gravity scales with $\rho g a^3$ where ρ is the density and g is the acceleration due to gravity. These two forces balance when the $a = l$, where l is the capillary length given by $l = \sqrt{\gamma/\rho g}$.¹⁵ When $a < l$, surface tension dominates over gravity, and the droplet is spherical. When $a > l$, gravity is more important, and the droplet becomes flatter. For water near $100\ ^\circ\text{C}$, the capillary length $l \approx 2.5\ \text{mm}$. The initial radius of our droplets was about $1.34\ \text{mm}$, so the drops initially appear to be quite spherical and the eccentricity is measured to be about 0.2. As the droplets shrink, they became more spherical as the effect of surface tension becomes even more important relative to that of gravity. Eventually, the measured eccentricities increase as shown at $t = 27\ \text{s}$ in Figure 1. The upturn in measured eccentricity is likely caused by droplet buckling and is defined to be the time of buckling, t_b . Values of t_b also convey information about the relative sizes of the droplets at the time of buckling. The reason for this is that all droplets began drying at nearly the same volume and all droplets were observed to dry at nearly the same rate, regardless of the PEO molecular weight or PS size. Therefore, larger values of t_b correspond to smaller droplet volumes at buckling.

Bulk Rheology. We performed bulk rheology experiments to better understand the mechanical properties of solutions containing both PS and PEO at elevated temperatures. These measurements were performed with a stress-controlled rheometer (Malvern CVOR) using a 40-mm-diameter cone and plate tool with an opening angle of 4° . The rheometer was equipped with a temperature control unit that maintained the sample at $85\ ^\circ\text{C}$, as close as experimental conditions allowed to the expected droplet drying temperature of $100\ ^\circ\text{C}$. To prevent evaporation of the water during the measurement, the sample and tool were covered by silicone oil AR 20 (Fluka). Samples contained PS particles of $110\ \text{nm}$ radius obtained from IDC.

In our experiments, the rheometer provided a sinusoidal shear stress and measured the response of the material. The in-phase component of the response, G' , yields the real part of the modulus

and is a measurement of the elasticity of the system. The out-of-phase component of the response, G'' , is a measurement of the viscosity of the system. The ratio $\tan \delta = \{G''\}/\{G'\}$ gives a measure of the relative solid to liquidlike nature of the system, whereas $G^* = \sqrt{G'^2 + G''^2}$ is the magnitude of the complex modulus and gives a measure of the total resistance to deformation, both elastic and viscous. Values of $\tan \delta$ and G^* were measured using a peak stress of $0.1\ \text{Pa}$ at $0.1\ \text{Hz}$. This frequency corresponds to a time scale of $10\ \text{s}$, which is of the same order as the time of drying of the single drops (roughly $40\ \text{s}$). When included, the PS concentration was $2\ \text{wt}\ \%$, or 10 times the initial weight percent of PS in the single-droplet experiments. This corresponds to the average expected weight percent of PS after the droplet volume shrinks by a factor of 10, which is a reasonable representative buckling volume. Tests were performed using a wide range of PEO concentrations, with 10 times the initial concentration of PEO in the droplets ($0.05\ \text{wt}\ \%$) being near the middle of the selected range. It was possible to measure high concentrations of $M_w = 10^3$ and 10^4 PEO because all measurements were performed at $85\ ^\circ\text{C}$, well above the melting temperature of these materials.

Results and Discussion

Spray Drying. Images of spray-dried powders obtained by SEM reveal that changing the molecular weight of PEO in the PS suspensions has a dramatic effect on the morphology of the dried powder as seen in Figure 2. Powders formed with no PEO are nearly spherical yet slightly buckled, as shown in Figure 2a. The average diameter of the granules was measured by image analysis to be about $3.2\ \mu\text{m}$. Powders formed with PS and low-molecular-weight PEO had an average size of $2.4\ \mu\text{m}$ yet were more crumpled in appearance, as shown in Figure 2b. The largest and most crumpled powders were formed using high-molecular-weight PEO and had an average diameter of about $3.8\ \mu\text{m}$ as shown in Figure 2c.

From the measured powder sizes and the initial concentration of the particles, we estimate that the initial diameter of the droplets formed in the spray drier was roughly $20\text{--}30\ \mu\text{m}$. Performing single-droplet experiments on droplets of this size would be extremely difficult because of rapid drying and difficulties with visualization and confinement. Therefore, our single-droplet experiments were performed on droplets roughly 2 orders of magnitude greater in size than the droplets used in the spray-drying experiments. Despite this difference, we expect the basic mechanism of buckling to be similar in the two experiment types because droplet buckling appears to be governed by interparticle

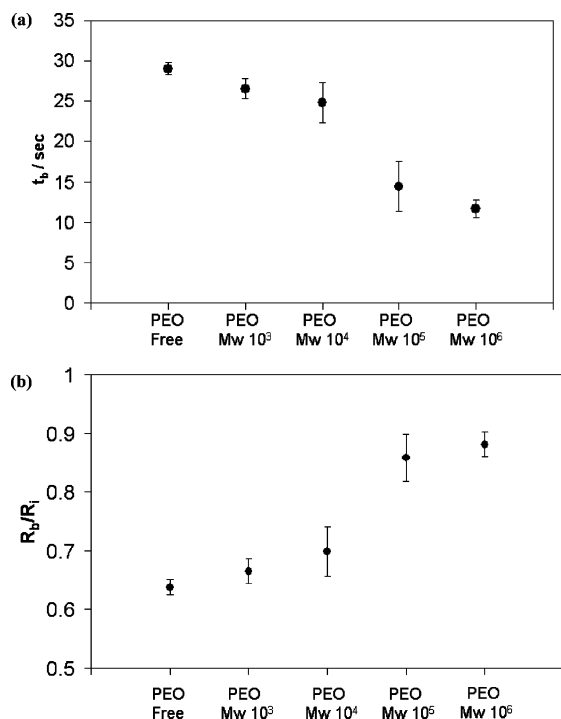


Figure 3. (a) Buckling times of droplets containing PS–PEO suspensions. (b) Radius, R_b , of the droplets at the time of buckling, normalized by the initial droplet radius, R_i . The PS particles had radii of 110 nm.

forces.⁸ Moreover, the size of the droplet at buckling relative to the initial size has been shown to be independent of the initial droplet size, albeit in the millimeter size range.⁸

In general, increasing the molecular weight of the polymer caused the granules to be larger and more crumpled. Did the high-molecular-weight PEO cause the outer layer of particles to be weaker and therefore more susceptible to buckling? To understand how the different morphologies may have evolved in the spray-drying experiment, it is useful to visualize the buckling behavior of the drying droplets directly by observing single droplets suspended by the Leidenfrost effect above a hot plate.

Buckling of Single Droplets. Droplets deposited on a hot plate and suspended by the Leidenfrost effect exhibited a wide range of behavior. Of these, perhaps the most useful to study is buckling, which signifies the transition to solidlike properties. The study of buckling can also offer insight into why some spray-dried samples have more crumpled morphologies. Buckling was observed in all droplets containing PS.

Experiments were performed using PS particles of radii 110 and 1000 nm. For both particle sizes, we observe that as the molecular weight of PEO increases the droplets buckle sooner and at larger volumes (Figure 3). The PEO-free droplets buckled at the smallest sizes and showed the largest values of t_b . Low-molecular-weight PEO samples had t_b values close to those of PEO-free droplets. Samples with high-molecular-weights PEO buckled at the largest radii and had lower values of t_b . Figure 3b shows the droplet radius at buckling, R_b , normalized by the initial droplet radius, R_i . In our experiments, we did not vary the initial droplet size because previous work has shown the ratio R_b/R_i to be independent of particle size.⁸

The fact that droplets containing high-molecular-weight PEO buckled sooner and at larger sizes than those containing low-molecular-weight PEO may be useful in understanding the more crumpled morphologies of the high-molecular-weight PEO samples in the spray-drying experiments. It seems likely that in

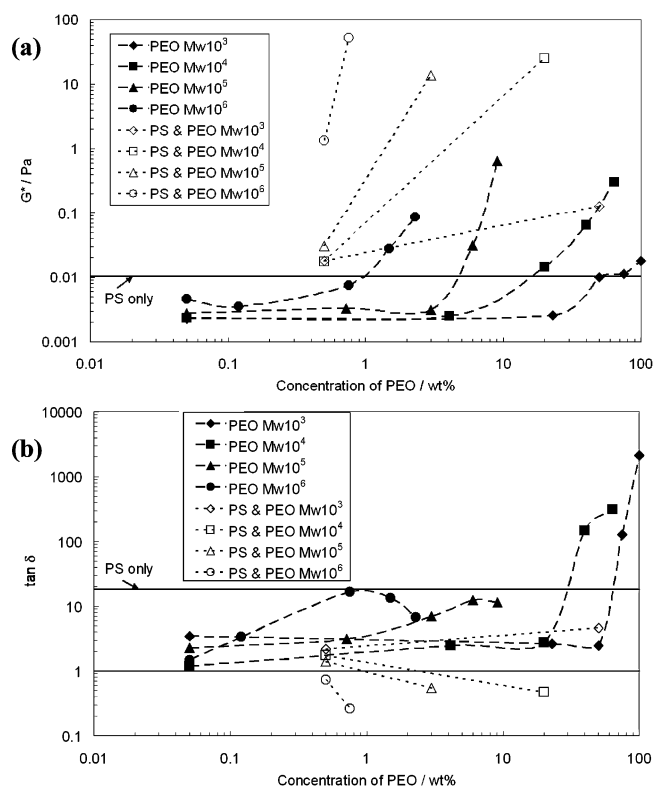


Figure 4. Viscoelasticity of PEO–PS mixture. (a) Samples containing both PS and PEO (open symbols) have higher combined elastic and viscous resistance (G^*) to deformation than samples containing only PS (solid line) or only PEO (closed symbols). Increasing either the molecular weight or concentration of PEO causes G^* to increase. (b) Samples containing both PS and PEO are more elastic ($\tan \delta$ is lower) than samples containing only PS or only PEO. Increasing either the molecular weight or concentration of PEO causes the PS–PEO suspensions to become more solidlike.

the spray-drying experiments samples containing high-molecular-weight PEO underwent a liquid to solid transition earlier in the drying process than the samples with low-molecular-weight PEO. Once the material deposited on the outer edge of the droplet by the receding interface became solidlike, the droplet could accommodate further shrinkage only by buckling, resulting in the crumpling of the outer shell. Thus, more crumpling would have occurred in the samples that buckled sooner. The crumpled morphology is also a function of the material properties of the solidlike shell. Shells that buckle earlier in the drying process are expected to be thinner than those that buckle later because the receding interface has swept out less droplet volume.⁸ These thinner shells are likely to be more amenable to wrinkling and deformation. Given the agreement between the single-droplet experiments and the spray-drying experiments, it appears that the single-droplet experiment is a useful model for spray drying.

Because single-droplet experiments required less material than spray-drying experiments, it was feasible to experiment with two different sizes of PS particles. Samples containing PS particles of radius 1000 nm generally buckled later than samples containing PS particles of radius 110 nm and equivalent amounts and molecular weights of PEO. This is in agreement with previous results showing that droplets with larger charge-stabilized particles buckle later than droplets with smaller particles of the same type.⁸ Although spray-drying experiments were performed only on an intermediate particle size of 350 nm, we would expect, on the basis of single-droplet experiments, that decreasing the particle size would produce more crumpled morphologies in spray drying due to earlier buckling.

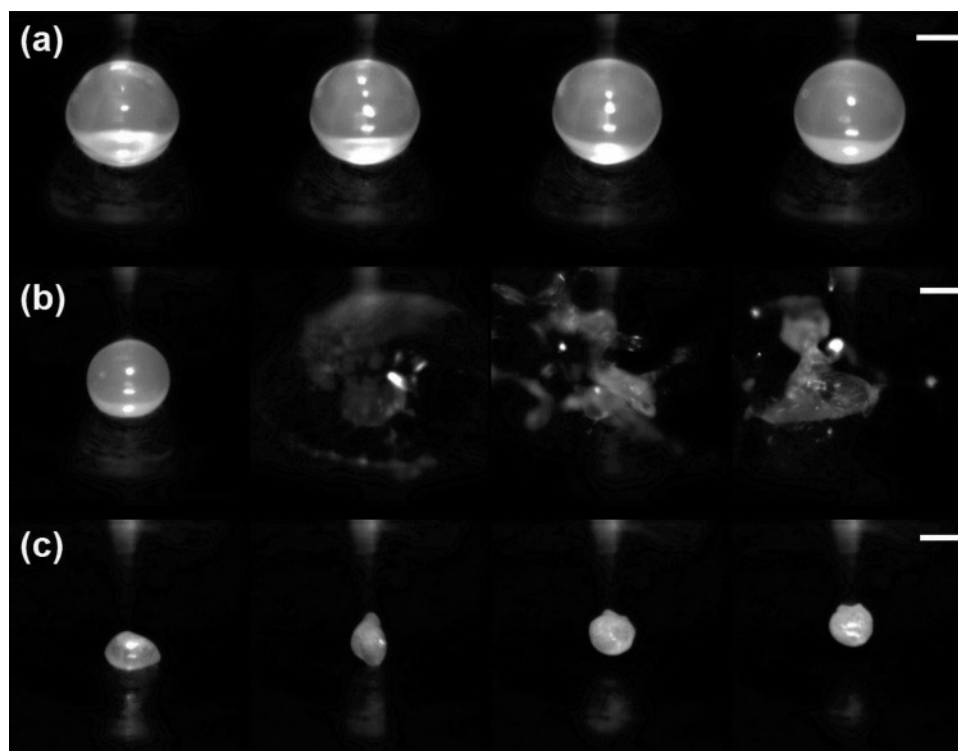


Figure 5. Droplet rippling, exploding, and jumping. The scale bars represent 1.0 mm. (a) Rippling motions of a droplet containing PS and high-molecular-weight PEO ($M_w = 10^6$). Adjacent snapshots are separated by 0.04 s. (b) The sudden violent explosion of a droplet containing PS and high-molecular-weight PEO ($M_w = 10^6$). Adjacent snapshots are separated by 0.02 s. (c) Jumping of a droplet containing PS and low-molecular-weight PEO ($M_w = 10^3$). Jumping occurred several times during drying, both before and after buckling. Adjacent snapshots are separated by 0.02 s.

Viscoelasticity of the PS and PEO Mixture at High Temperature. We performed bulk rheology experiments to better understand the viscoelastic properties of PS and PEO at elevated temperatures that govern the observed deformation behavior.

Our data show that the presence of even small amounts of PEO can have a significant effect on the rheology of PS suspensions. Values of G^* measured from samples containing both PS and PEO (open symbols, Figure 4a) tended to be several orders of magnitude greater than G^* measured from samples containing only PS (solid line) or only PEO (solid symbols). Figure 4a also shows that increasing both the molecular weight and the concentration of PEO can cause G^* to increase dramatically. Values of $\tan \delta$ (Figure 4b) show that samples containing both PS and PEO (open symbols) are more elastic ($\tan \delta < 1$) than samples containing only PS (solid line) or only PEO (solid symbols). Samples with high-molecular-weight PEO were more elastic than samples with low-molecular-weight PEO. All but the lowest-molecular-weight sample become more elastic as the PEO concentration increases. The crossover from viscous to elastic behavior (taken to be $\tan \delta = 1$) happens at lower concentrations of PEO for the high-molecular-weight PEO solutions than for the low-molecular-weight PEO solutions.

The elastic nature of the PS/PEO mixtures is likely due to the PEO-mediated flocculation of PS particles.⁹ PEO becomes less soluble in water at temperatures higher than the lower critical solution temperature (LCST). For PEO in water at the saturated vapor pressure of water, the LCST was found to lie between 156 and 172 °C for molecular weight 3350 (depending on the concentration) and between 102 and 106 °C for molecular weight 10^5 .¹⁶ Therefore, at 85 °C the high-molecular-weight PEO will be less soluble than the low-molecular-weight PEO and may be more likely to cause particle flocculation. PEO-mediated flocculation of PS particles may be further enhanced by bridging

interactions, caused by the binding of the same PEO to two different PS particles.^{10,17} This effect should also be more prevalent in samples with high-molecular-weight PEO.

These measurements are useful in interpreting the buckling behavior of evaporating liquid droplets, where the average concentration of polymer in the droplet is continuously increasing during evaporation. Given that increasing the molecular weight of PEO in a suspension reduces the stability of the particles, we would expect the higher-molecular-weight samples to become solidlike and buckle earlier than low-molecular-weight samples. This is exactly what was observed in the hot plate experiments where buckling occurred sooner (t_b was lower) for droplets of higher molecular weight. Although our rheology data is in qualitative agreement with our spray-drying and single-droplet experiments, it is difficult to make a quantitative comparison because the rheology data does not allow us to quantify the particle–particle repulsions required for making an estimate of the critical buckling radius.⁸ However, bulk rheology is still useful in learning about how the ingredients of the suspension affect the mechanical properties, thus aiding in the interpretation of observed mechanical deformation.

Ripples, Explosions, and Jumps. In addition to buckling, we observed qualitatively new droplet behavior in single-droplet experiments performed on samples containing both PS and PEO. This behavior includes droplet rippling, violent droplet explosions, and droplet jumping. Observation of this behavior helps us gain further insight into the transient viscoelastic properties of droplets during drying.

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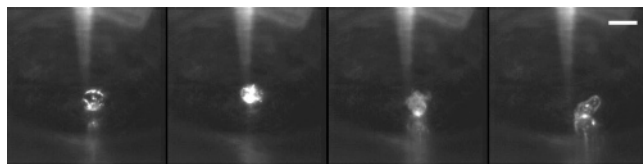


Figure 6. Plate contact and subsequent boiling of a droplet containing PEO ($M_w = 10^6$) solution and no PS. Adjacent snapshots are separated by 0.40 s. The scale bar represents 1.0 mm.

Rippling droplets are periodically covered by small waves that originate from the bottom of the droplet as shown in Figure 5a.

Exploding droplets suddenly and violently break into numerous smaller droplets as shown in Figure 5b. The explosion appears to originate at the bottom of the drop. After the explosion, a portion of the droplet often remains attached to the plate, where it continues to boil away.

Jumping droplets suddenly spring into the air above the hot plate to heights of about one droplet diameter. Jumping is shown in Figure 5c.

Movies showing exploding, rippling, and jumping are available online. From a careful examination of high-speed videos, we believe that this behavior is caused by droplets directly contacting the hot plate surface because of the loss of the Leidenfrost effect. If this is indeed the case, then the loss of the Leidenfrost effect appears to be temporary in the case of rippling and jumping.

In the case of droplets containing PS without PEO, no rippling, jumping, or explosions were observed. By contrast, in the case of droplets containing only PEO without PS, the droplets eventually lost the Leidenfrost effect and contacted the hot plate directly, causing the water in the droplets to boil away rapidly as shown in Figure 6. Droplets containing high-molecular-weight PEO contacted the plate sooner than droplets containing low-molecular-weight PEO.

In droplets containing PS particles of radius 110 nm, jumping was primarily observed in droplets containing low-molecular-weight PEO ($M_w = 10^3, 10^4$). It was common for a given droplet to jump two to three times over the course of the experiment both before and after buckling occurred. Droplets with both PS particles of radius 110 nm and high-molecular-weight PEO ($M_w = 10^5, 10^6$) showed quite different behavior. Rippling occurred in the early period after droplet deposition on the hot plate and before buckling. Droplet explosions occurred only after droplet buckling. Droplets containing PS particles of radius 1000 nm exhibited only jumping behavior, for all molecular weights of PEO.

The observed behavior may yield insights into the viscoelastic properties of the drying droplets. The rippling behavior appears to be more fluidlike than solidlike and occurs early in the drying process. Jumping and explosions are more solidlike behavior and occur later in the drying process. When the Leidenfrost effect is lost, the droplets make contact with the hot plate directly, and the water within the droplets begins to boil, causing rapid expansion and deformation within the droplet. When the droplet shell is more liquidlike (before buckling), the shell is able to accommodate the sudden onset of boiling with rippling motions. When the shell is more solidlike (after buckling), the shell may not be able to deform quickly enough to accommodate the expansion due to boiling, which may cause the droplet to explode. In the lower-molecular-weight PEO samples, when the droplet loses the Leidenfrost effect before or after the time of buckling, the shell almost seems to explode, but there is apparently just enough viscous dissipation in the shell to accommodate the expansion and the droplet stays together and exhibits jumping.

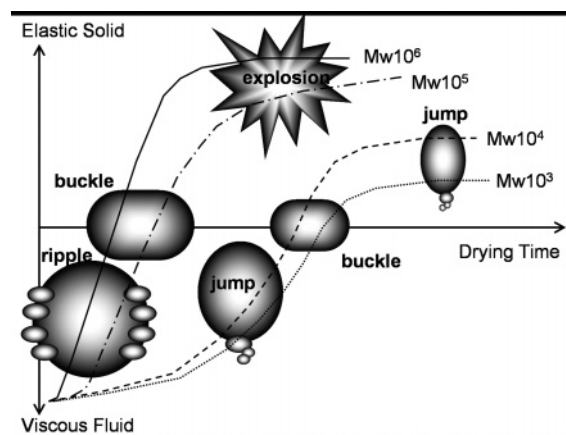


Figure 7. Schematic showing how the viscoelastic properties of a droplet may influence droplet behavior when the droplet loses the Leidenfrost effect. The vertical axis represents the viscoelasticity of the droplet shell, and the horizontal axis represents the drying time. Buckling signals the droplet's transition from liquidlike to solidlike. Droplets with high-molecular-weight PEO transition from liquidlike to solidlike sooner than those with low-molecular-weight PEO. When a liquidlike droplet containing high-molecular-weight PEO contacts the hot plate, it ripples. When a more solidlike droplet of the same type contacts the hot plate, it explodes. When droplets of low molecular weight contact the hot plate, they exhibit a jumping behavior that is intermediate between rippling and exploding. This jumping behavior is observed both before and after buckling.

These ideas are illustrated schematically in Figure 7. Once the droplets become very small near the end of their drying time, many samples do eventually contact the plate and boil away.

Conclusions

We have investigated the effect of the molecular weight of PEO on the drying behavior of colloidal PS suspensions by conducting spray-drying experiments, single-droplet experiments, and bulk rheology experiments. The spray-drying experiments showed that droplets containing high molecular weights produced powders that were larger and more crumpled in appearance. This is supported by single-drop experiments showing that droplets of high molecular weight buckled early in the drying process while they were large, as opposed to droplets of low molecular weight that buckled later in the drying process when they were smaller. Finally, bulk rheology experiments showed that samples containing high-molecular-weight PEO are more solidlike and therefore are expected to be more susceptible to buckling. Additional behavior observed in single-droplet experiments offers further insight into the mechanical response of the viscoelastic droplets that are subjected to boiling when droplets lose the Leidenfrost effect and contact the underlying hot plate directly.

We have demonstrated that changing a single ingredient parameter, the molecular weight of PEO, can dramatically change the morphology of spray-dried PS powders. Changing the molecular weight of PEO tunes the particle–particle interactions and thus changes their viscoelastic properties during drying.

In contrast to our simple two-ingredient model system, industrial drying processes can involve many ingredients and even more possible varieties of a given ingredient, such as the molecular weight distributions of the polymers employed. The design and testing of spray-drying formulations is a daunting task both from a practical and theoretical standpoint. Our results underscore the potential usefulness of single-droplet experiments for studying and designing industrial drying processes and formulations. Single-droplet experiments can provide physical insights into the mechanisms of drying that give rise to the final

powder morphologies. As these mechanisms become better understood, single-droplet experiments could eventually become a powerful tool for testing the effect of solution ingredients on spray-dried powder morphologies. Current development of spray-drying processes and ingredients often involves performing large-scale spray-drying experiments and then characterizing the resulting powders with methods such as SEM. In contrast, dozens of single-droplet experiments can be performed in a single day on a simple experimental setup without using large quantities of ingredients. These experiments could be used to probe many variations of ingredient parameters quickly to find promising ingredient combinations that can be further studied with the more time-intensive techniques. Such a strategy could lead to new

spray-drying formulations and save time and energy in the development process.

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Supporting Information Available: Movies showing the rippling, exploding, and jumping behavior of single droplets that are drying while being suspended above a hot plate by their own vapor. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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