Solvent Retention and Crack Evolution in Dropcast PEDOT:PSS and Dependence on Surface Wetting

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ABSTRACT: The drying of nanocolloidal polymers is governed by the interplay among surface tension, evaporation, and contact-line pinning, among other phenomena. Here, we describe the sequential evolution of poly-3,4-ethylenedioxythiophene:poly(styrene sulfonate) (PEDOT:PSS) through two distinct regimes evidenced by annular or radial cracking and show that the cracking dynamics and solvent-retention postdrying and postcracking are mediated by wetting to the substrate surface. The corresponding changes in the PEDOT:PSS morphology are also observed to relate to the radial or cracking dynamics. It is suggested that the wetting-dependent effect offers a route to control morphology, understand solvent retention, and reduce cracking in polymer latex films. This study highlights the importance of substrate choice, an underexplored area of investigation in the study of colloidal materials.

INTRODUCTION

Cracking phenomena are observed in practically every colloidal solid, from the largest mudflats to small blood traces in medical diagnosis to the almost-microscopic trails deposited in inkjet printing. Most interest in cracking behavior aims to eliminate cracks to improve electrical, optical, or other material performance, but the same dynamics can also be harnessed as a tool for self-assembly, for example, toward large-area transparent conductive nanostructures. This study describes crack patterns observed in dropcast poly-3,4-ethylenedioxythiophene:poly(styrene sulfonate) (PEDOT:PSS) toward improved lab-to-lab repeatability and predictive control of the complex polymer dynamics. The aim of this study is to provide a cogent description of the trends to mediate the surface dynamics and point to morphological issues related to surface wetting. We intend to advance specific understanding of this conducting polymer and to contribute to the study of colloidal drying in general.

There are several useful properties of PEDOT:PSS, including high electrical conductivity, good optical transparency, mechanical flexibility, and coating stability over time. Moreover, because PEDOT:PSS films simultaneously exhibit high electrical conductivity and low thermal conductivity, progress is being made in the application of PEDOT:PSS as a thermoelectric material. Cracking behavior compromises these useful properties. Internal stresses built up during the drying process also reduce material performance, even if cracking does not occur. This study examines the accumulation of tensile and compressive stresses at different points in the drying process, mediated by the contact angle with the substrate.

Specific cracking and deposition phenomena have been identified in drying colloids. Research continues to investigate both basic drying mechanisms and the effects the drying process has on the properties of the resulting film. One of the most intensively studied is the coffee-ring effect, in which solids are deposited in a ring when the contact line between the droplet and the substrate is pinned. As a result of this pinning, liquid flows toward the outer edge of the droplet to replace the liquid lost through evaporation, carrying with it the suspended particles.

The Marangoni flow is another well-known effect: a concentration or temperature gradient within a droplet leads to a surface energy gradient, resulting in fluid flow toward the region of higher surface tension. This effect has been found to oppose and even reverse the coffee-ring effect to yield a film with maximum thickness at the center. The interplay between the coffee-ring and Marangoni effects is not yet fully understood.

Colloids have been found to dry in a four-stage process, with flow effects like those mentioned above dominating in the “submerged phase”. During the “wet” and “moist” phases, after the liquid has receded below the level of the solid material surface, drying behavior is largely determined by capillary forces on the solid—liquid interfaces. In this paper, we clearly observe the existence of the submerged and wet phases in a drying colloid. We characterize the cracks that form in each phase both on the centimeter scale and by scanning electron microscopy (SEM).

One important type of colloid is the latex (plural: lattices), defined as an aqueous colloidal dispersion of polymer particles. It is a conductive polymer latex that is studied in this paper.

Received: January 15, 2018
Accepted: February 5, 2018
Published: April 5, 2018
Lattices have a number of advantages compared to other polymer forms for industrial applications: they can be processed at room temperature and using a variety of inexpensive processes, including inkjet printing,\(^3\) silkscreening,\(^12\) and spin-coating.\(^29\) Using aqueous dispersions also avoids the safety and health issues associated with volatile organic solvents.\(^4\) Many different polymers can be produced in latex form by emulsion polymerization.\(^4\) Nanoparticle lattices are particularly exciting because they allow for nanomaterial self-assembly, using simple bottom-up processes.\(^30\) Nanoparticle lattices have been used to generate plasmonic nanomaterials,\(^31\) photonic crystals,\(^32\) and various kinds of metamaterials.\(^33\) PEDOT:PSS is one of the most widely used conducting polymers, in part because it is available as a latex and therefore has the processing advantages described above.\(^11\) Nanopatterned PEDOT:PSS films have already shown some promise as photonic materials\(^14\),\(^34\),\(^36\) and as improved anodes for solar cells.\(^36\) Our knowledge of the self-assembly dynamics of PEDOT:PSS nanostructures advances the feasibility of nanotechnology in optical and electronics applications.

In this paper, we report on the drying behavior observed in dropcast PEDOT:PSS films, on glass slides and on flexible polymer substrates. The different wetting properties of the substrate surfaces are found to have a strong effect on the evaporation and film formation processes. The percentage mass lost after drying is found to be lower on less wettable surfaces, indicating higher water retention. Annular and radial cracking regimes are observed. Annular cracks are found to predominate on the more wettable glass substrate and at higher evaporation rates. Radial cracks, propagating from the edge of the film to the center, are found to dominate on the polymer substrate and in thicker films. The radial cracks are hypothesized to be the result of mud-cracking when the film thickness exceeds the maximum crack-free thickness \((h_{\text{max}})\). The annular cracks are attributed to the stick-slip motion of a pinned contact edge.

We provide several guides relevant to crack prevention in PEDOT:PSS films during colloidal deposition: higher temperatures and humidities are found to prevent annular cracking; film thickness, which varies with contact angle, mediates the cracking, particularly with high thicknesses; and radial cracking occurs largely with high contact angles. Modification of the substrate surface and alteration of the drying conditions are feasible techniques for altering or preventing cracking behavior. Corresponding differences in the PEDOT:PSS morphology are also observed with varied drying dynamics. The dependence of cracking on wetting shows the importance of substrate choice in colloidal deposition experiments, an underexplored factor in self-assembly investigations.

### RESULTS AND DISCUSSION

Figure 1 illustrates a subset of the crack patterns observed in dropcast PEDOT:PSS films. Figure 1a–c are prepared under ambient conditions, whereas Figure 1d is dried in vacuum. The evolution of these patterns and stress dynamics associated...
Evaporation rate data and time-lapse images obtained for distinctly radial and circular cracking processes are shown in Figure 2. Insets show the representative propagation of cracks on more than two dozen film samples. Cracks occur at short intervals in the evaporation curve. Drying occurs more rapidly on the more wettable substrate: droplets deposited on glass reach equilibrium after approximately 180 min, whereas similarly sized droplets deposited on vinyl reach equilibrium after 270 min. The substrates also influence the moisture content retained: the total mass loss is lower when the samples are deposited on vinyl substrate as compared to that on glass: 58 versus 97% for the plotted samples. Higher moisture retention is attributed to the lower surface-area-to-volume ratio of the droplets at higher contact angles. The thicker film may also result in an outer, dried layer, which seals the film surface, preventing further evaporation.

In the case of radial cracking, the evaporation rate or mass flux curve exhibits two distinct regimes. Initially, the mass flux decreases linearly with time as the liquid volume decreases. In a second stage, there is a rapid drop in the evaporation mass flux, which we observe in the radially cracked samples after 55% drying (Figure 2). When the film reaches equilibrium with its environment, the mass flux drops to 0. Time-lapse images of this sample show macroscopic contractions of the liquid meniscus between the initial deposition time and 55% drying (225 min). The meniscus then recedes beneath the surface of the deposited polymer film, and cracks propagate from the edge of the film to the center. These stages are consistent with the submerged, wet/moist, and “dry” phases of a drying latex film described by Roberts and Francis.21

The trend in the mass loss rate for circular cracking is discontinuous, with roughly linear periods of drying punctuated by sudden drops in the mass loss rate. The sharp drops in mass loss rate occur when the contact lines move. A steep fall is seen after 90% drying, corresponding to the contraction of the meniscus to the surface of the solid film. The circular cracks form earlier in the drying process than do the radial cracks. The circular cracking process is not observed at temperatures above 22 °C or at humidities above 85%.

A comparison of the radial and annular cracks under SEM (Figures 3 and 4) crucially reveals differing polymer morphologies associated with the two cracking processes. The radial cracks, which occur on a more hydrophobic surface, appear as sharp discontinuities in a thick polymer film. In contrast, the circular cracks, formed on a more hydrophilic surface, exhibit a thin PEDOT:PSS film separating two thicker films around a circular crack. The high-magnification image in Figure 3 shows a distinct granularity to the radially cracked film, with flattened PEDOT:PSS grains, which is not apparent in the high-magnification image in Figure 4 with the circularly cracked PEDOT:PSS.

In analyzing these results, we describe the evolution of the radial and annular cracks as separate processes and relate these processes to the results described above. We connect our investigation with prior work and conclude with a description of the crack patterns shown in Figure 1. Our observations indicate that radial cracking occurs via shear stress in a more compact, rigid film, whereas the stress underlying the annular striping occurs over a longer duration via tension in a more humid and pliable film. Because the morphology of the PEDOT:PSS grains is influenced by polymer stress far before cracking, our investigation shows different nonlinear regimes of stress in the polymer film that are solely influenced by substrate or surface wetting, which deserves further study.

The radial cracking process is a strain-limited process, as illustrated in Figure 5. As the meniscus of the droplet contracts, the polymer particles are displaced by van der Waals and capillary forces and form a random close-packed structure. As the meniscus contracts further, capillary forces build up between the particles. The response of the particles to this force depends on their shear modulus;20 hard particles remain in place to form films with significant void fraction, whereas soft particles deform to occupy the space vacated by the moving meniscus. Previous studies on PEDOT:PSS structures indicate that soft particle deformation does occur in the drying of PEDOT:PSS,37,38 where the PSS material merges together to fill voids,39 which we also observe in our SEM images (Figures 3 and 4). Once the particles are strained completely, filling the void space, the contraction force acts to rupture the film, forming cracks. Because the meniscus contracts toward the center of the droplet/film, the particles at the outside edge are the first to deform completely. Hence, the cracks would be
Subsequently limit the derived by Tirumkudulu and Russel, and the middle partially because the edge of the hydrophobic case because the smaller droplet radius gives rise to radial cracks are not observed. Radial cracking dominates in the packing. Equation 1 indicates the maximum thickness at which the particles reduces the void fraction of the film composed of hard particles.

By understanding the competing dynamics, radial cracking may be reduced by controlling the drying conditions, like temperature and humidity, or changing the substrate wetting, which affect the coffee-ring and Marangoni effects and subsequently limit the film thickness. A relation for the critical cracking thickness of low-shear-modulus particle lattices is derived by Tirumkudulu and Russel:

\[ h_{\text{max}} = \frac{37\gamma}{GM_{\text{ff}}(1 - \phi_{\text{cc}})} \]  

where \( \gamma \) is the liquid surface tension, \( G \) is the shear modulus of the particles, and \( M \) and \( \phi_{\text{eq}} \) are, respectively, the coordination number and particle volume fraction of spheres in random close packing. Equation 1 indicates the maximum thickness at which radial cracks are not observed. Radial cracking dominates in the hydrophobic case because the smaller droplet radius gives rise to thicker polymer films. The cracks propagate from the edge to the middle partially because the edge of the film is the thickest, which is attributed to the coffee-ring effect. Radial cracking can coexist with circular cracking if the outer ring grows beyond \( h_{\text{max}} \) before contact-line depinning occurs. In this investigation, the film thickness is primarily determined by substrate–droplet interactions, with higher contact angles leading to increased droplet heights and therefore thicker films. Substrate surface modification offers a route for the production of crack-free dropcast films by modification of the film thickness by tuning the contact angle. However, our results also show that cracking can occur in thin films by tension-mediated processes that are not explained by eq 1, as seen in the circular cracking and the propagation of radial shrinkage cracks from thinner parts of the film in Figure 1b.

In contrast to the radial cracking dynamics, there is not a clear relation governing pinning and cracking as there is for radial cracking, that is, eq 1. A few recent works highlight the importance of drying-mediated dynamics in annular rings, and the drying dynamics at the coffee ring can lead to strong self-assembly. We infer that a new relation would need to be derived to describe a different cracking transition, which is observed in Figure 6. We observe that annular cracking is a tension-limited process and occurs in the submerged phase, as illustrated in Figure 4. The droplet edge is pinned by frictional forces between the latex and the substrate. As evaporation occurs, the droplet flattens, increasing the surface area. The surface energy increases, opposing the pinning force. The surface energy can eventually exceed the pinning force, resulting in stick-slip motion of the contact line toward the center. This stick-slip motion leads to the formation of an annular outer deposit and a circular inner deposit, connected by a minimal PEDOT:PSS film deposited during the motion itself. Shrinkage of the inner and outer deposits then results in the formation of the circular crack. Partial circular cracks are observed in some samples. This is observed to be the result of uneven pinning behavior: in some samples, surface contaminants led to inhomogeneous pinning. In other cases, substrates placed on slightly sloping surfaces are found to crack preferentially on the elevated side; gravitational forces can depin the contact line. On the hydrophobic substrate, the forces of repulsion between the droplet and the surface are sufficient to prevent pinning, thereby preventing the formation of circular cracks. The crack spacing is dependent on surface wetting and increases when the substrate is more hydrophilic. This can be interpreted from volume conservation considerations.

## SUMMARY AND CONCLUSIONS

We have demonstrated that the radial and annular crack morphologies are the result of two separate evolving colloidal processes. Both of these cracking behaviors can occur simultaneously during drying and depend on droplet morphology and evaporation behavior and therefore are mediated by the droplet–substrate and droplet–atmosphere interfaces. Alternately, the environmental parameters such as aggregation and aging, which influence latex viscosity, can arrest cracking.

The two cracking regimes occur in two different drying phases and result in different cracking patterns (Figure 1a–d). In Figure 1b, the coffee-ring effect results in the thickness at the edge that exceeds the maximum crack-free thickness, where radial shrinkage cracks occur after the formation of an annular crack.

Figure 1d shows a film prepared under vacuum. In this case, the stick-slip motion occurs multiple times, resulting in a concentric structure of alternating thick and thin stripes. This modulation and the resulting striped structures may be of interest for the generation of patterned PEDOT:PSS films. Contact-line pinning results from microscopic surface rough-
ness on the substrate. The mechanisms of contact-line pinning are yet to be fully understood. 41

Although radial cracking may be well understood, the annular cracking behavior is less scrutinized and also less commonly observed; the interplay between the Marangoni, drying, and pinning dynamics is more certainly complex. The morphology of PEDOT:PSS, which is related to the capillary forces and surface tension of and between the latex particle, not only varies with batch, but also evolves during drying, influencing the cracking process. Nevertheless, a more thorough evaluation of the effects shown here, probing the drying conditions on the contact-line motion, could provide new routes for self-assembly toward the generation of patterned films, such as multilayer bands separated by monolayers, of PEDOT:PSS or other dropcast-able materials, as shown in Figure 1d. Theoretical modeling of the Marangoni dynamics would be essential in future research efforts to these ends.

The cracking dynamics studied here are relevant to our understanding of the morphology of PEDOT even when cracking does not occur. Here, we have also shown that the liquid retention in the drying behavior changes depending on the surface wetting. Moreover, the direction or alignment of the grains of the PEDOT:PSS and their morphology appear to be influenced by the shear or tension-related stress. Future research may compare the influence of surface wetting on the grain morphology further, with particular attention to the potential for modulated self-assembly that occurs via competing nonlinear complex drying dynamics.

* EXPERIMENTAL SECTION*

The PEDOT:PSS films are prepared by dropcasting on clean glass (Globe Scientific 1405-10, 24 × 24 × 0.21 mm3) and plastic coverslips (Pella 2225, 22 × 22 × 0.18 mm3, poly(vinyl chloride)). The coverslips are rinsed thoroughly with acetone, methanol, and isopropyl alcohol and blown dry with nitrogen. The PEDOT:PSS (Sigma-Aldrich, 0.5% PEDOT, 0.8% PSS in water) is placed in a 3 mL cuvette, sealed with parafilm, and sonicated for 10 min prior to dropcasting.

The substrates are placed on the pan of a digital balance (Torbal AGCN200) and the measurement is tared. A fine-tip plastic transfer pipette is used to deposit approximately 0.25 g of latex on the center of the substrate. A webcam and Chronolapse software are used to take time-lapse images of the substrate and for mass readout at regular intervals throughout the drying process. Droplet profiles are imaged immediately after deposition with a digital camera. To investigate drying under vacuum, the droplet is deposited on a substrate placed in the vacuum chamber of a plasma cleaner (Harrick PDC-326). The use of this apparatus precluded the collection of mass flux data or time-lapse images.

The annular cracking behavior is found to be sensitive to aging of the PEDOT:PSS material, as well as to ambient temperature and humidity. Circular cracking is not observed at humidities above 85% and is not consistently observed when ambient temperatures exceeded 27 °C. Several weeks after the PEDOT:PSS bottle is opened, aging of the PEDOT:PSS prevents the circular cracking.

Scanning Electron Microscope (SEM) images are produced using FEI Quanta 2000.

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**Notes**
The authors declare no competing financial interest.

*ACKNOWLEDGMENTS*
The authors gratefully acknowledge funding from NSF-DMR-1151783.

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