Structure Formation During Drying of Polymer Dispersions

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The drying of polymer dispersions is typically described as a three-stage process, encompassing the evaporation of water until the particles touch (stage I), the coalescence of the particles (stage II), and polymer interdiffusion, leading to tough film (stage III).[1] The contribution deals with the implications of *spatially heterogeneous drying*. Firstly, there is vertical gradient of water content, which can lead to an accumulation of particles at the top of the film.[2] Secondly, there is a lateral drying front moving inwards from the edge to the center of the drop. The lateral drying front entails:

- a movement of particles from the center to the rim ("coffee stain effect")[3]
- a movement of dust particles entrapped at the air/water interface from the rim to the center
- a stress wave propagating from the rim to the center.

Using a flexible membrane as the substrate for drying droplets and imaging the membrane distortion as a function of time, we have obtained maps of the in-plane stress exerted by the

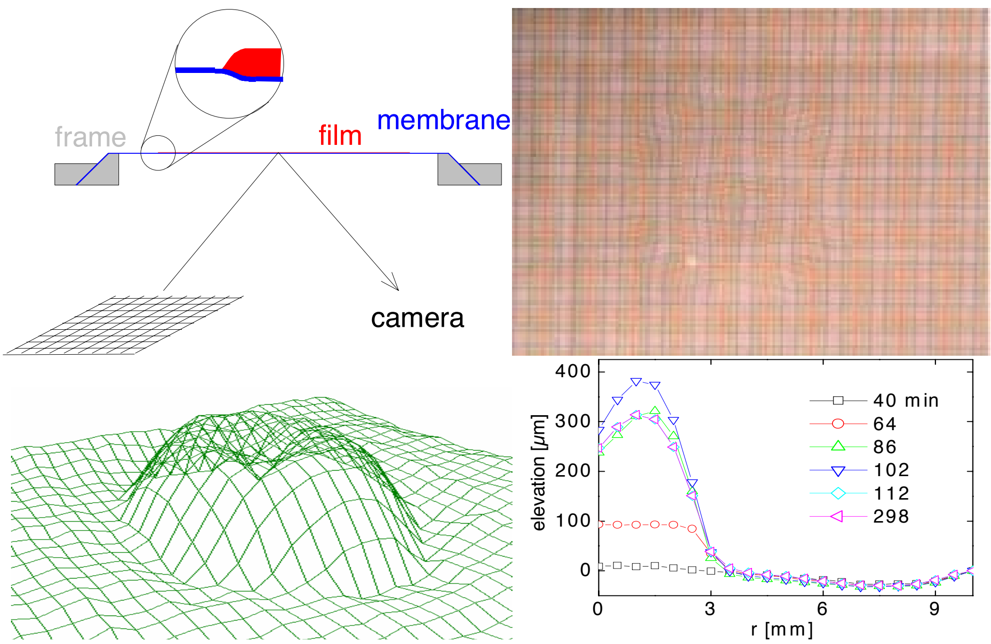

Fig. 1. Scheme of measurement (upper left)), raw data (upper right), stress distribution (lower left), and radially averaged stress distribution as a function of time for a drying droplet of a polymer dispersion (lower right).

drying drop onto the membrane (Fig. 1). There usually is a maximum of stress at the rim of the drop. In some cases, the stress decays, but in others, this stress pattern persists (lower right in Fig. 1). The stress front can lead to a flow of material from the center to rim which is not related to the classical coffee stain effect. The flow is driven by the stress gradient, rather than evaporation. For thick droplets, this kind of stress evolution even leads to cracks in the center (Fig. 2a), rather than cracks emanating from the rim, which is the more common case[4,5] (Fig. 2b). When the stress front reaches the center, stress relaxation by an outward movement of material is frustrated and cracks therefore are initiated.

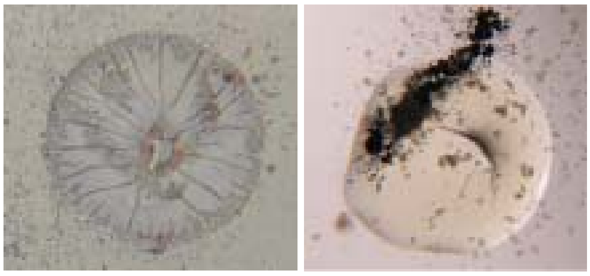

Fig. 2 Cracking patterns.
Top: Usual form with cracks emanating from the rim.
Bottom: Droplet with a crack in the center. Dust particles were deposited on top of the drop to visualize the lateral movement of material.

These findings highlight the complex interplay of spatially heterogeneous diffusion, surface tension, stress, and stress relaxation for the drying of complex materials.

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