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Introduction

In coating technologies such as spin-coating or flow-coating, a liquid containing polymers or colloids is spread on a surface and a deposit is left upon drying. Unfortunately, drying often occurs while the contact line of the liquid is advancing on the solid surface, causing the contact line to be temporarily pinned on the substrate, leading to a non homogeneous deposition of the polymer or colloid layer. Our study concerns this topic, which fundamental interest comes from the fact that there is a non trivial coupling between evaporation and the hydrodynamics of an advancing contact line. Indeed, the hydrodynamics diverges at the contact line and the evaporation rate diverges at the contact line causing the formation of a very viscous zone at the edge of the drop. Our goal is to understand 1- how the motion of the contact line is influenced by the nature of the polymer deposit formed upon drying 2- how the polymer deposition is influenced by the advancing motion of the drop. These two phenomenon can induce the contact line to undergo a stick-slip instability in the case of colloidal suspensions [1] i.e. the advancing droplet is alternatively pinned and unpinned on the substrate.

In this study we present the case of a hydrosoluble polymer of variable molecular weight and concentration. We show that the polymer deposit that is left by evaporation does not strictly pin the contact line of the advancing drop. Instead, we observe alternative phases where the contact line slowly slips on the substrate (a few microns per second) or rapidly advances (several mm/s).

Experimental

We use solutions of a water-soluble polymer, polydimethylacrylamide, of various concentration (between 0.1 and 30%) and molecular weight (between $50 \cdot 10^3$ and $1300 \cdot 10^3$ g/mol).

In order to study the coupling between evaporation and hydrodynamics, we have set up an experiment where a droplet of polymer is let to dry for a time, τ_{drying} , between 5 minutes and 1 hour inside a box where the relative humidity can be tuned easily between 10 and 90%. After the drying phase, the drop is inflated with a syringe pump at a constant flow-rate. During the inflation time, the displacement of the contact line as well as the contact angle of the drop on the glass substrate during pinning-unpinning transitions of the drop, which are related to the force causing the contact line to pin on the substrate are recorded with a CCD camera.

Results

During inflation, the droplet of polymer does not undergo a true stick-slip instability as for colloidal suspensions. Instead, the contact line slowly slips ($v_{\text{pin}} = 1\text{-}100 \mu\text{m/s}$) on the substrate while the contact angle increases. Once the contact angle reaches a maximum value θ_m , the drop spreads rapidly ($v_{\text{unpin}} \approx$ several millimeters per second) on the substrate and the contact angle returns rapidly to its initial value (Fig. 1)

In order to understand the mechanism which pins the contact line during the inflation, we have investigated the parameters that control v_{pin} as well as the variations of the contact angle θ .

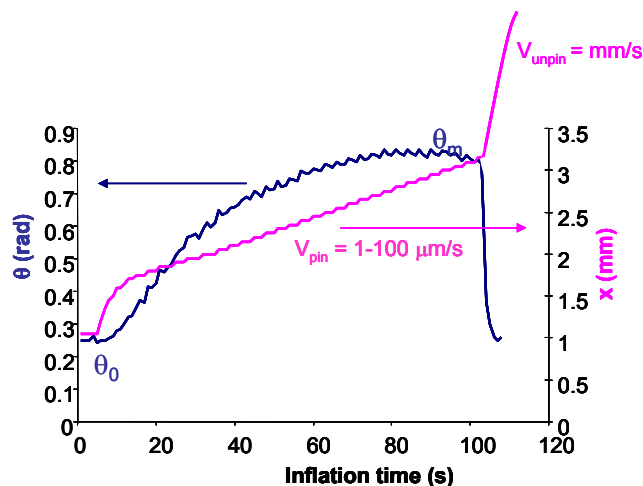


Fig. 1. Evolution of the contact angle and the position of the contact line during a stick-slip event

We find that the relative humidity plays a major role in the pinning process confirming that the stick-slip instability is controlled by the competition between evaporation and hydrodynamics.

Moreover we find that for semi-dilute solutions, the variations of the contact angle upon pinning-unpinning transitions depend on the polymer concentration but not on the molecular weight. We interpret this result as a sign that the pinning mechanism is not caused by the divergence of the viscous stress at the edge of the drop.

By studying independently the kinetics of drying (contact angle and drop radius during evaporation), we find that the contact line recedes during drying and leaves a polymer ring around the drop. We show that during the inflation, as the droplet advances on the polymer deposit, the pinning force increases until the contact line reaches the edge of the polymer deposit. Once in contact with the glass substrate, the droplet spreads rapidly and the contact angle decreases. We show that the pinning mechanism strongly depends on the size of the deposit, which is controlled by parameters such as the relative humidity, the drying time or the concentration.

1. E. Rio *et al.*, *Langmuir*, 22, 7, 2006