Spreading of volatile oils on swelling hydrophobic polymer brush layers

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Polymer brush layers swell fully in good solvents and partly in ambient vapor of good solvents. The spreading of volatile liquids on brush layers is governed by subtle combination of hydrodynamic flow, vapor transport and swelling kinetics. We studied the spreading various alkanes on hydrophobic polymer brush layers of poly-lauryl-methacrylate (PLMA). A rich phenomenology is observed including the formation of a wide halo (see figure) with a gradient of the degree of swelling of the brush layer ahead of the slowly advancing contact line. Drop radius and halo width follow algebraic scaling laws for this system with a macroscopic contact angle of less than 1°. Depending on thickness and grafting density of the brush layer, advancing contact lines can also display a contact line instability. In general, contact line profiles evolve over many hours before achieving a steady state configuration that seems to be stabilized by continued very gradual evaporation of the reservoir drop. Experiments with variable connectivity of the substrate, controlled vapor concentration fields, as well as variable vapor pressure (variable chain length) demonstrate the relevance and relative importance of viscous flow, diffusive transport within the brush layer, as well as evaporation-condensation as competing solvent transport mechanisms.

Numerical calculations using gradient dynamics support the qualitative scenario and reproduce in a semi-quantitative manner the time-dependent swelling profiles in the halo region as extracted from interferometry measurements. In particular, the calculations confirm the relevance of a continuous evaporative flux for stabilizing the halo structure and for setting the degree of swelling far from the contact line. Matching of experiments and calculations allows to estimate solvent transport coefficients within the brush layers and at the brush-vapor interface.

We discuss potential applications of responsive oleophobic polymer brush layers as controlled oil transport layers in advanced grease-lubricated bearings.

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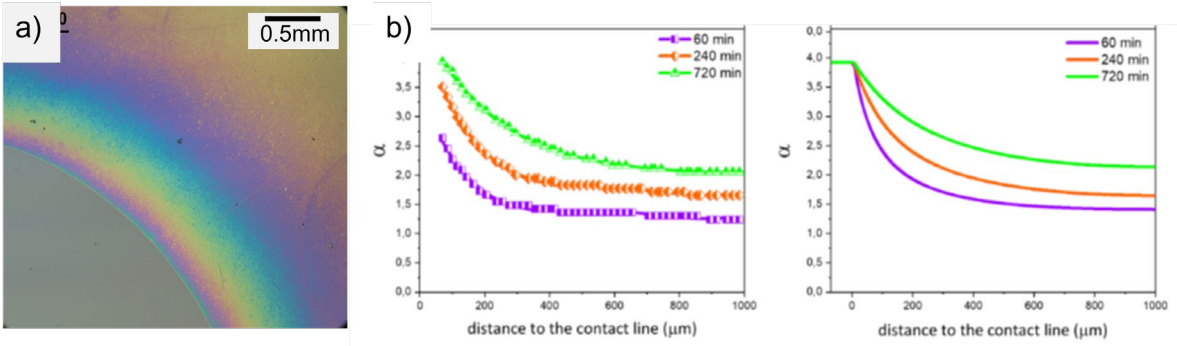

Figure 1. *Spreading drop of hexadecane on PLMA brush layer with halo ahead. a) white light top view. b) experimental (left) and numerical (right) halo thickness profiles as a function of distance from contact line after 60, 240 and 720min.*