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Dewetting and deposition of thin films with insoluble surfactants from curved silicone hydrogel substrates ☆

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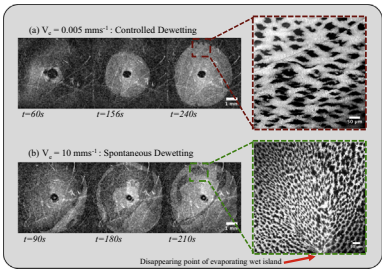
GRAPHICAL ABSTRACT



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ABSTRACT

We investigate the stabilizing effect of insoluble surfactant monolayers on thin aqueous films. We first describe an experimental platform that enables the formation of aqueous films laden with dipalmitoylphosphatidylcholine (DPPC) monolayers on curved silicone hydrogel (SiHy) substrates. We show that these surfactant layers extend the lifetime of the aqueous films. The films eventually "dewet" by the nucleation and growth of dry areas and the onset of this dewetting can be controlled by the surface rheology of the DPPC layer. We thus demonstrate that increasing the interfacial rheology of the DPPC layer leads to stable films that delay dewetting. We also show that dewetting can be exploited to controllably pattern the underlying curved SiHy substrates with DPPC layers.

1. Introduction

Drainage and dewetting dynamics of biological liquid films are prevalent throughout the human body. Prominent examples include the saliva in the oral cavity [1], pulmonary lung surfactants [2], and the tear film on our eyes [3]. This paper explores the last case, where the stability of the tear film is important to ocular comfort and protection of the corneal epithelium.

The tear film on our eyes is a thin (<10 μm) and complex multilayered lubricating structure. This film can be broadly classified into an aqueous layer burdened with an insoluble lipid layer. Together this structure achieves an average surface pressure in the vicinity of 25 mN m^{-1} [4]. However, precise details regarding the composition, thickness and functions of the these layers continue to be the subject of ongoing research [5–11]. In modern healthcare applications, a silicone hydrogel (SiHy) contact lens may be placed on the corneal surface, resting in the aqueous phase as shown in the schematic in Fig. 1. During the duration of a blink-cycle, the tear film diminishes in thickness due to the action of

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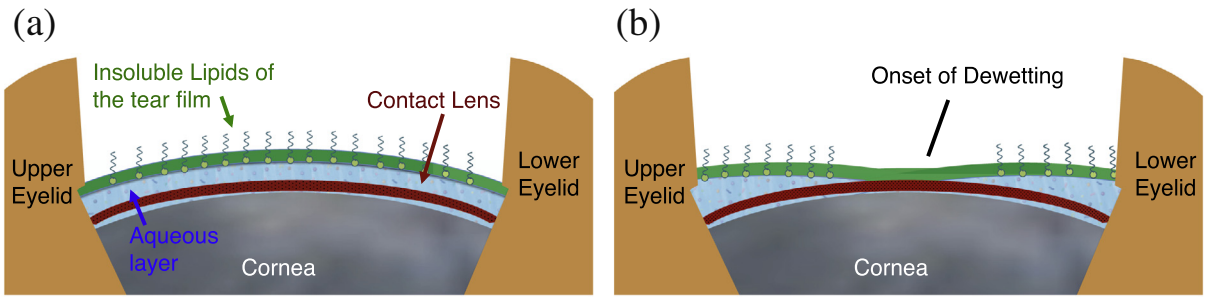

Fig. 1. Schematic (not to scale) illustrating the dewetting of the tear film in the presence of a SiHy contact lens on our eyes.

simultaneous evaporation, and osmotic and capillary flows, resulting in a thin film that can potentially break up and dewet on the anterior surface of the contact lens. This tear film dewetting subsequently leads to depositions of naturally occurring tear film constituents and is an ongoing clinical problem with acute ophthalmological repercussions including symptoms of dry eyes and reduced vision for the contact lens wearer [12–15].

Modeling the dewetting of the tear film is challenging due to its complexity and the various processes involved. It is thus beneficial to begin with simplified models that can be systematically augmented. We start with an experimental model that consists of a simple aqueous subphase layered with a monolayer of insoluble material. We choose dipalmitoylphosphatidylcholine (DPPC) due to its extensive use as an analog tear film phospholipid [16–20] and its well studied phase behavior and interfacial rheology [21,22].

It has been shown that insoluble lipid layers possessing significant interfacial rheology retard drainage and stabilize thin films [23]. Excellent review articles that cover decades of research on thin-film stability [24], thin-film dynamics [25], wetting and spreading [26], and role of structural forces on dewetting films [27], are available. However, the role of interfacial rheology in dewetting dynamics has received less attention [28–30].

Dewetting of liquid films can be accompanied by the deposition of constituents, both soluble and insoluble, and can provide a means for controlled patterning of surfaces [31,32]. Previous work on dewetting and deposition has almost exclusively considered planar, rigid surfaces. This paper concerns the dewetting of surfactant-laden aqueous films from curved, soft surfaces and the subsequent deposition of these surfactant layers. The surface rheology of the insoluble layers is systematically varied and shown to influence the onset of dewetting. We further highlight our ability to vary the morphology of the depositions by controlling the drainage process leading up to dewetting.

2. Materials and methods

2.1. Silicone hydrogel (SiHy) lenses

We use a single type of commercial SiHy soft contact lens for this study: PureVision (Balafilcon A, Bausch & Lomb, Rochester, NY). Low dioptric power of −0.50 lenses are chosen to ensure uniform thickness across the lens surface. To leach out blister-pack surfactants, we use the following protocol. Using soft Nylon tweezers, we carefully transfer the lenses into a glass vial containing 5 mL of phosphate buffer solution (PBS, Gibco Life Technologies, Grand Island, NY). This vial is then gently agitated at room temperature for 20 min. The lenses are then transferred to a second vial containing fresh PBS and subject to further agitation for 20 min. Finally, the lenses are transferred to a third vial with fresh PBS and agitated over-night.

As disclosed by the manufacturer, PureVision lenses are silicone hydrogels with 36% water-content and 64% principal monomers that include N-vinylpyrrolidone (NVP), tris(trimethylsiloxysilyl) propylvinyl carbamate (TPVC), N-vinyl amino acid and poly (dimethysiloxy) di (silylbutanol) bis(vinyl carbamate) (PBVC).

2.2. Insoluble materials and fluorescence microscopy

For the dewetting experiments, DPPC is procured from Avanti Polar Lipids Inc. (Alabaster, AL) in 25 mg mL^{-1} vials. We create stock solutions of 1 mg mL^{-1} in chloroform (Sigma–Aldrich, St. Louis, MO), which are kept in a freezer until required.

For the deposition experiments and fluorescence imaging, DPPC is doped with Texas Red 1,2-dihexadecanoyl-sn-glycero-3-phosphoethanolamine, triethylammonium salt (TR-DHPE) (Avanti Polar Lipids). We choose a recipe of 99 mol% pure DPPC and 1 mol% TR-DHPE [33–35].

To visualize the lipid deposition patterns on the SiHy substrates, we carefully slice each lens into four quadrants. We then sandwich each quadrant between a clean glass slide and a coverslip. To prevent desiccation of the lens samples, we first fill the excess gap between the coverslip and slide with PBS and then we seal the edges of the coverslip with clear nail polish. Fluorescence images were obtained using a two-photon laser scanning microscope (Ultima IV, Prairie Technologies, WI) fitted with a titanium:sapphire laser (Mai Tai HP Deep See, Spectra Physics,CA). An upright water-immersion 20X objective (0.9 numerical aperture, XLUM Plan Fl W, Olympus) was used in conjunction with a green filter (Chroma Set 49005).

2.3. Surface pressure-area isotherm and interfacial shear rheology

To measure the surface pressure versus area isotherms, DPPC is spread at the air–water interface in a Langmuir trough by touching microdrops of lipid stock solution (1 mg mL^{-1}) using a clean Hamilton syringe. We use deionized-distilled water as the subphase from a Milli-Q filtering system (EMD Millipore, Billerica, MA) with a resistivity of 18.2 MΩ cm and surface tension of 72 mN m^{-1}. The surface pressure is monitored using a platinum Wilhelmy plate connected to a surface pressure sensor (KSV NIMA Ltd., Helsinki, Finland). The volume of DPPC spread is $\sim$ 35 μL, and the spreading pressure is less than 0.5 mN m^{-1}. After chloroform is allowed to evaporate for 15 min, the interface is compressed using symmetric Teflon barriers at a speed of 1.5 cm^2 min^{-1}.

We use an interfacial shear rheometer (KSV NIMA Ltd., Helsinki, Finland) to measure the interfacial shear rheology of DPPC [36,37]. We follow the protocol described in detail previously [23,38]. All the measurements are conducted at room temperature (23 ± 1 °C) and at a frequency of 1 Hz.

2.4. Experimental setup: i-DDrOP

To conduct dewetting experiments, we use the Interfacial Dewetting and Drainage Optical Platform (i-DDrOP) developed