## Wetting Behaviors on Viscoelastic Coating Surface

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This presentation reviews our research on the wetting of an acrylic, thermoplastic elastomer developed as an adhesive for wound binding applications.<sup>1</sup> The polymer is generated via solvent polymerization and undergoes multiple thermal stripping operations to remove residual solvent, unreacted monomers and other contaminants. It is composed primarily of the monomer 2-ethylhexyl acrylate and has a glass transition temperature of less than -50 °C. Data from rheological analysis demonstrate that the polymer is exceedingly soft with a strong tendency to dissipate elastic energy. Cast films from the polymer are smooth with typical rms roughness values around 60 nm. The purity and high viscoelasticity of these films make them ideal for examining how surface deformation impacts wetting behavior. As will be discussed, wetting-ridge deformation on the polymer for a variety of liquids is significant and substantially modifies both static and dynamic wetting processes.

Figure 1a shows a sequence of frames for the evaporation of a 5  $\mu$ L sessile drop placed on a thin film of the polymer. As water evaporates under ambient conditions, drop volume is reduced but the contact line remains fixed allowing the contact angle to decrease to 0°. Upon complete evaporation, the drop leaves behind a clearly visible pattern with a perimeter consistent with that of the initial drop (Fig. 1b). Figure 1c summarizes the reverse process, i.e., addition of water to the drop. It can be seen that the original contact line is maintained as the drop volume is slowly

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increased. This increases the contact angle from 100° to greater than 150°. Eventually, the drop collapses with liquid from the top surface spilling around the outside of the contact line to establish a new line with an angle again near 100°.



**Figure 1.** (a) images taking at various times during the evaporation of a sessile drop: (b) an optical profilometer image of the polymer surface subsequent to evaporation: (c) images taken during the addition of water to a sessile drop, which eventually forces its collapse.

The process of adding water to the drop to force failure at the wetting line reveals how the three-phase line translates when pinned by a deformation ridge. We refer to this process as "stick and break". If a smooth expansion of the drop radius is to occur, movement is forced by the requirement that the deformation ridge be translated along with the wetting line. Given the highly dissipative nature of the polymer, the capillary energy is not sufficient to prompt such motion. Movement occurs only after the volume of the drop becomes too large to be supported by the meniscus resulting in its failure and release of drop liquid to establish a new three-phase line. The stick-and-break mechanism is distinct from the previously reported "stick and slip" wetting behavior, for which the three phase line is distorted by the presence of topological defects or chemical heterogeneities.<sup>2</sup>

The stick-and-break mechanism is also found to have a significant influence on dynamic wetting processes. Figure 2a is a typical setup for Wilhelmy plate experiments. The polymer coated plate is advanced into the test liquid at a constant rate. The measured force exerted on the

plate is determined by the liquid surface tension and contact angle at the liquid-plate interface. Figure 2b is an optical image of the coated plate after it has been advanced into water at a rate of 0.2 mm/min. A series of parallel wetting deformations are clearly visible. These are deformation ridges each with an approximate height and width of 6  $\mu$ m and 400  $\mu$ m, respectively, and separated along the plate by about 1 mm. Figure 2c is the corresponding variation of the force-displacement diagram for the plate during its advancement. The abrupt changes of the force curve display a quasi-periodic variation with a period and total number of cycles that corresponds to the separation distance and number of ridge structures induced on the plate, respectively. The series of sharp vertical decreases (jumps) in the magnitude of force are associated with break events while the steady increases in force which follow are associated with subsequent sticking processes.



**Figure 2** (a) diagram of setup for Wilhelmy plate experiments: (b) The wetting ridge pattern formed on the coated plate during advancement: (c) and the corresponding force–displacement curve. (The numbers indicate the corresponding wetting ridges and force peaks.)

In the data from these experiments, a number of variables can be identified for characterizing the process including the magnitude (height and width) of the formed ridges, ridge separation distance along the plate (pinning distance) and the maximum decrease in the magnitude of the force during pinning events (pinning force). As will be discussed in this presentation, a systematic study was carried out in which plates coated with the acrylic polymer were wet with a variety of liquids over a range of plate speeds. In general, pinning distances were found to decrease with increasing wetting rate. This data is well fit by a power-law function: dropping sharply in the low rate region and more gradually at higher wetting rates. Force-displacement curves were also found to change with wetting rate, transitioning from distinct quasi-periodic capillary force oscillations at lower speeds to more chaotic oscillations and then eventually becoming smooth for higher rates. The extent to which this behavior was observed, if at all, appeared to be determined primarily by the viscosity of the wetting liquid.

Receding measurements were also impacted by the stick-and-break process. Forcedisplacement curves for Wilhelmy experiments in water using a plate coated with the polymer exhibited quasi-periodic capillary force oscillations in both advancing and receding, with the receding force oscillations having significantly smaller amplitudes. For paraffin oil, the-stick and-break mechanism was apparent during advancement but not recession. For measurements at a silicone oil–air interface, force-displacement curves for both advancing and receding were smooth and overlapped, indicating no pinning events and no hysteresis, respectively. At the water-silicone oil interface, the curve was smooth during the advancing, while quasi-periodic force patterns consistent with stick-and-break motion were apparent during the receding.

In summary, the wetting systems highlighted in this presentation demonstrate that contact line movement on the surfaces of soft materials can propagate through the stick-and-break mechanism. The extent to which this mechanism is demonstrated depends on properties of the substrate, fluids, and interfaces formed. It is proposed that both adhesion and wetting can be manipulated in complex manners through careful control of the identified variables.

## **References:**

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