**Wilhelmy balance characterization beyond contact angles: differentiating leaching from
nanosurface reorganization and optimizing surface modification**

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Abstract

Over and above measurements of contact angles, this article provides examples from our work that emphasize unexpected wetting behavior using the Wilhelmy Plate (WP) method. These findings either would not have been noticed by conventional sessile drop methods or might have been dismissed due to deviations associated with measurements or sample-to-sample variations in surface composition. The examples chosen for this article include: (1) Wilhelmy plate force distance curves providing a sensitive measure for the detection of leaching or diffusion of species from polydimethylsiloxane elastomeric coatings, (2) A Dynamic Contact Angle (DCA) investigation of a polyurethane to establish whether changes in CAs vs immersion time were due to leaching of substances that changed the surface tension of water or to nanosurface reorganization of polymer chains, (3) Changing network formation conditions that give low or high receding contact angles (θ_R) and “sticky or slippery” wetting of water drops on a widely used Sylgard 184 silicone coating as well as the impact of θ_R on ice adhesion and (4) Polymer surface modification for introducing special functionality via a modifier is shown to depend on a balance of miscibility and immiscibility that resulted in an unexpected “more is less” dependence on concentration for a fluorous modifier and a condensation cured silicone.

1. Introduction. Placing a water drop on a polymer surface provides a simple method for characterizing wettability of the outermost surface of a polymeric material. The water drop spreads if the surface is hydrophilic while it “beads up” if hydrophobic. To gain a semi-quantitative knowledge of the interaction of a water drop with a surface, tilting the substrate on which the drop rests or adding/removing a water drop enables measurements of advancing, θ_A , and receding, θ_R , contact angles (CAs), which are defined by the three phase contact line: water, air and polymer surface. Herein, we describe an alternative to sessile drop CAs, the Wilhelmy Plate (WP) balance or tensiometer for evaluating wetting behavior.[2] The “value added” for this method is exemplified by (a) sensitive evaluation of leaching that leads to contamination (b) characterization of “sticky” vs. “slippery” poly(dimethylsiloxane) elastomers from receding contact angles and (c) tracking a blend approach to surface modification. We note at the outset that roughness and superhydrophobic surfaces are not subjects for this review.

A conventional method for Wilhelmy Plate dynamic contact angle measurements has been used as described by Andrade, Ober, Tretinnikov and DeSimone.[3-6] The immersion of coated coverslips is depicted in Figure 1. The immersion of a hydrophobic coating with water surface tension resisting wetting is shown in Figure 1A. Figure 1B shows the immersion of a hydrophilic coating with water wicking onto the substrate driven by forces including hydrogen bonding.

A sensitive electrobalance provides characteristic mass or force distance curves (fdc’s) from which θ_A and θ_R are obtained by extrapolation. Figure 2A shows an fdc for a flamed glass coverslip. Superposition of fdc’s is found if the glass and the water surface are free of contaminants. To illustrate the WP method for a conventional polymer glass, Figure 2B shows

Figure 1. A. Immersion (θ_A) and emersion (θ_R) of a hydrophobic coating: **1**, initially in air; **2**, water contact; **3, 4**, increasing immersion; **5**, emersion. **B.** Immersion (θ_A) and emersion (θ_R) of a hydrophilic coating; the immersion and emersion sequence is the same as **A**.

curves for a polymethylmethacrylate coating.[7] Contact angles were independent of cycle with θ_A , 78°; θ_R , 56°, which are similar to those previously reported by sessile drop methods.[8-10]

Over and above measurements of CAs, this article provides examples from our published work that emphasize unexpected wetting behavior provided by the Wilhelmy plate method.

These findings either would not have been noticed by conventional sessile drop methods or might have been dismissed due to inaccuracies associated with measurements or sample-to-sample variations in surface composition. The WP examples chosen for this article include:

(1) A sensitive technique for the detection of leaching or diffusion of species from Pt-cured silicone coatings

(2) An expansion to detection of leachates comprising a DCA investigation as to whether changes in CAs vs immersion time were due to leaching of substances that changed the surface tension of water or to nanosurface reorganization of polymer chains.

(3) The effect of changing network formation conditions that gives “sticky or slippery” wetting of water drops on a widely used Sylgard 184 silicone coating as well as the impact of θ_R on ice adhesion.

(4) Application of DCA to polymer surface modifiers (SMs) for introducing special functionality shed light on the balance of miscibility and immiscibility that led to “more is less” compositional dependence for a fluorous PSM and a condensation cured silicone.

McCarthy[11] has treated of CA analysis including the importance of understanding theoretical and practical aspects of θ_A , θ_R and contact angle hysteresis, $\theta_A = \theta_A - \theta_R$. This insight and pioneering work of Johnson and Dettre[12] into the phenomena of contact angle hysteresis is basic to understanding unexpected findings mostly from DCA measurements. Where

Figure 2. **A**, DCA for a flamed glass coverslip show repeated superposition of fdc's for immersion and emersion cycles indicating no detectible contamination of the coverslip or the water surface. **B**, Three superposed fdc immersion and emersion cycles for poly(methyl methacrylate). (Thermo-Fisher).

appropriate, unexpected findings from DCA were followed up with characterization by sessile drop CA measurements, Attenuated Total Reflectance-Infrared (ATR-IR) spectroscopy and Tapping Mode-Atomic Force Microscopy (TM-AFM) imaging to provide mechanistic insights.

2. Contact angles for Poly(dimethylsiloxane) (PDMS) elastomers influenced by leaching.

We initiated work ~20 years ago to clarify the wetting behavior of PDMS materials.[13, 14] Problems encountered obtaining reproducible sessile drop CAs led to experiments with the Wilhelmy plate method.[15]

Model hydrosilylation-cured coatings were prepared using a molecular crosslinker $\text{Me}_n\text{Si}(\text{OSiMe}_2\text{H})_{4-n}$ ($n = 0$, “XH₄” or 1, “XH₃”) and divinyl terminated PDMS with Si-H to vinyl ratios ~ 1.5 / 1. The optimum ratio was established empirically by determining the Si-H to vinyl ratio that produced a PDMS network with negligible Si-H IR absorption and minimum hexane-extractable sol.[16] The results described herein focus on networks from “C-PDMS”, a commercially available α,ω -divinyl PDMS with MW 28kDa.

Representative DCA fdc curves for a C-PDMS coating are shown in Figure 3A. The first advancing force vs. distance curve (fdc-a₁) gives $\theta_A = 116^\circ$. The three subsequent advancing fdc's give $\theta_A = 107^\circ$ while all of the receding fdc's yield $\theta_R = 88^\circ$.

The abrupt change in θ_A from the first (116°) to the second and subsequent cycles (107°) and the constant value for $\theta_R = 88^\circ$ was reproducible for many samples and other Pt-cured PDMS coatings. The first clue to the cause was the observation of hysteresis when the post-test water was interrogated

with a flamed coverslip (Figure 3B). This result stands in contrast that in Figure 2A, which shows repeated superposition of immersion and emersion cycles indicating no detectable contamination of the water surface. The results in Figure 3B were attributed to water

Figure 3. A, Four DCA cycles for a Pt-cured C-PDMS coating; the first advancing fdc (fdc-a₁) gives $\theta_A = 116^\circ$. **B,** Three DCA cycles using a flamed coverslip with the post-test water from **A.** (Cahn)

contamination by leachates. Leaching of PDMS cyclics and linears from PDMS elastomeric materials is well known.[17-21]

Fdc's such as that shown in Figure 3B are often seen as students take several days to master the flaming technique that removes contaminants from the water container and a bare cover slip. After 2-3 days, some become doubtful that results shown in Figure 2A are possible but the "flaming" skill is finally acquired.

The contamination problem was also evidenced by DCA cycles for a fresh coating using the post-test water such as that from the test shown in Figure 3A. Force distance curve fdc-a₁ was not obtained but the fdc was identical to fdc-a₂₋₄ shown in Figure 3A. Increasing the surface area of the water reservoir slowed down the contamination of the water surface (Figure 4). Two advancing cycles ($\theta_A = 120^\circ$) and one receding fdc ($\theta_R = 82^\circ$) were observed prior to an irreversible change during fdc-r₂. The contact angles for cycles 3 and 4 were $\theta_A = 110^\circ$ and $\theta_R = 89^\circ$.

The onset of the fdc "collapse" midway along fdc-r₂ (Figure 4) is taken as evidence for formation of a coherent film on the water surface. Using this hypothesis, an estimate can be made for the amount of siloxane-containing species released from samples. Assuming a monolayer-like film and using covalent and Van der Waals radii, a 1 nm thickness is calculated.[22] For the 12 cm² surface area vessel (a 50 ml beaker), only 1 µg of siloxane-containing species is required to form a monolayer, while 8 µg is required for the larger vessel (74 cm²). Given a typical coating thickness (~0.2 mm) and area in contact with water (31 cm²), 8 µg is ~0.05% of the coating mass.

Our results may be compared with the determination of CAs by the captive bubble method. Kennan, et al., reported the wetting behavior of Silastic sheeting using both the underwater captive bubble and the sessile drop methods.[23] This material is a Pt-cured PDMS elastomer, but is filled with fumed silica (25%). The captive bubble method resulted in θ_A of 121-123°, while the sessile drop method gave $\theta_A = 112-115^\circ$. During the captive bubble

Figure 4. DCA fdc's for a C-PDMS coating with a vessel surface area 74 cm². (Cahn)

technique, leached siloxane-containing species would have to travel against gravity to reach the interface between the air bubble and water. This geometric arrangement works against contamination of the water-air interface and may account for the observation of θ_A similar to ours. An opposite arrangement exists for the sessile drop method, where the lower density siloxane-containing species can travel quickly to the water drop surface. The systematically lower θ_A reports using the sessile drop method may thus reflect contamination of the drop surface.

Perutz *et al* used the sessile drop technique on hydrosilylation cured PDMS films that had been extracted in toluene ($\theta_A = 118^\circ$ and $\theta_R = 90^\circ$). [24, 25] CAs are the same as our DCA result indicating that extraction of cured PDMS samples results in contamination-free contact angles. In our hands, wrinkling and debonding of a toluene extracted coating precluded DCA measurements.

3. CA dynamics for polyurethane in water: leaching or surface reorganization?
Polyurethanes are widely used for coatings and applications driven by mechanical properties. For biomaterials applications both mechanical and surface properties make

polyurethanes attractive.[26] In fact commercially available “biomedical grade” polyurethanes are often employed as biomedical materials. Recent examples include polyurethane interactions with lipoproteins[27] and a study the diffusion and partitioning of NO in biomedical polyurethanes.[28]

DCA measurements that showed leaching from Pt-cured PDMS elastomers affected water surface tension / CAs prompted examination of laboratory-prepared coatings of a linear thermoplastic polyurethane (TPU), 4,4'-(methylene-bis(*p*-cyclohexyl isocyanate))-butanediol(30)/ poly(tetramethylene oxide)(2000) or HMDI-BD(30)/PTMO(2000) **1**. Results on this model polyurethane were anticipated that would be relevant to applications as biomaterials and food and drug packaging.

Figure 5A shows fdc's for a coating of as-prepared **1**. Seven DCA cycles were obtained in succession. Each complete cycle takes about 3 min giving a total immersion time of ~20 min. DCA with a clean (flamed) glass coverslip (Figure 5B) shows hysteresis loops characteristic of water contamination due to leaching from as-prepared coating **1**.

Polyurethane **1** was purified by dissolution in tetrahydrofuran (THF) followed by precipitation into methanol / water (several times). A coated slide gave DCA results shown in Figure 5C. Differences compared to Figure 5A include a 7° higher θ_R and a post-test check characteristic of negligible water contamination (Figure 5D). Apparently, contamination of the water surface has a greater effect on θ_R compared to θ_A , which is increased by only ~4°.

Importantly, for reprecipitated polyurethane **1** the change in CAs after successive immersions is reversible after 5-10 min drying in air. X-ray Photoelectron Spectroscopy (XPS) and AFM studies demonstrate soft block concentration at the outermost polyurethane surface.[29-31] Thus, it is tempting to attribute the decrease in θ_A to weak water chemisorption, reorganization of the soft block and/or migration of the polar hard block to the surface.[32] However, the *increase* in θ_R is perplexing as the same model would suggest a *decrease* in θ_R as the surface becomes more polar (decrease in θ_A). Further studies are required to clarify the mechanism that accounts for decreasing θ_A but increasing θ_R . Such studies will be facilitated by the DCA as these changes in θ_A and θ_R are too subtle to be accurately assessed by sessile drop methods.

Current research is extending our report of polyurethane antimicrobial coatings based on polyurethane surface modifiers (SMs) having soft blocks with quaternary side chains.[33]

With a content of 2 wt% or less, these SMs “bloom” during processing and provided a desired antimicrobial surface functionality. A recurring issue in surface modified antimicrobial polymers is whether biocidal action is surface based (contact) or results from leaching of a biocidal species. As we move toward employing commercially available thermoplastic polyurethanes, characterization of these base polyurethanes by DCA becomes important so that we can eliminate leaching from the base polymer as a source of biocidal agent or species that could result in cytotoxicity.

4. Sticky or slippery Sylgard 184. Interest in platinum cured poly(dimethylsiloxane) elastomeric coatings led to surprising results from contact angle measurements on Sylgard 184.[1] This is a well-known resin system used for microfluidics and micromolding. [34, 35] In the course of studies on Sylgard 184, we observed that while cure conditions have little effect on advancing CAs, θ_A , strong effects are seen on receding CAs, θ_R . As shown in Figure 6, network formation at high temperature ($\sim 100^\circ\text{C}$) resulted in high θ_A 123° and high θ_R 85° . After network formation at low temperatures ($\leq 25^\circ\text{C}$) θ_A was still high but θ_R was $\sim 34^\circ$. An intermediate θ_R value (46°) was observed for cure at 60° . Contact angle hysteresis θ_A was $\sim 38^\circ$ for high temperature cured sample while that for low temperature cured one was $\sim 90^\circ$. Uncertainty about compositional effects on wetting behavior resulted in similar experiments with a model $\text{D}^{\text{V}}\text{D}^{\text{H}}$ silicone elastomer comprised of a vinyl terminated PDMS base and a polymeric hydromethylsilane crosslinker. Again, network formation at high temperature ($\sim 100^\circ\text{C}$) resulted in high θ_R , while low temperature cure retained high θ_A but gave low θ_R ($30\text{-}50^\circ$).

Figure 7. Contact angles by goniometry for Sylgard 184 coatings cured at **A**, 25°C ; **B**, 60°C and **C**, 100°C . [1]

The result obtained by using DCA was confirmed with the conventional goniometer with an LCD camera (Rame Hart). Deionized water ($\sim 18.2 \text{ M}\Omega$) was used as the probe liquid.

Sylgard 184 coatings are nanoscopically smooth and lack a contribution to contact angles from surface roughness.[36] Figure 7 shows water drop images for Sylgard coatings cured at three temperatures. Static drops and advancing / receding drops are shown along with CAs.

Static water CAs are about 10° lower than θ_A for DCA measurements and approximate those typically reported. Advancing / receding drop CAs show a trend similar to DCA measurements (Figure 6), although higher receding contact angles are found for 25 and 60°C cure.

These changes in θ_R translate to distinct effects on water adhesion. Considering a typical Pt cured Sylgard 184 coating with high temperature cure ($\theta_R \sim 84^\circ$) compared with one with low temperature cure ($\theta_R \sim 50^\circ$), practical work of water adhesion (w_a) for the samples cured at high temperature was ~ 1.5 times higher for the ones cured at low temperature. To explore the impact of this difference in w_a on water droplet flow, gradient coatings of Sylgard 184 elastomers were prepared by curing one end of a coated slide at high temperature and the other end at low temperature. Specifically, a drip coated microscope slide was cured over a thermal gradient from high ($\sim 200^\circ\text{C}$) to low ($\leq$ ambient) temperature. After 4 h the low temperature end was tacky so cure was completed at 100°C for 30 minutes. An θ_A of $\sim 120^\circ$ was observed over the entire surface (not shown), while a θ_R gradient was obtained reflecting Sylgard

184 network formation at three different areas (Figure 8). The high temperature end had θ_R of 88° while the low temperature end had θ_R of 38° . The θ_R for the middle was 51° (Figure 8A). Thus this coating has a gradient θ_R and a constant θ_A .

A water droplet roll-off test was used to characterize this distinctive gradient surface. Three water droplets of equal volume ($40\ \mu\text{l}$) were placed at the high temperature end, the low cure temperature end, and the middle of the coated microscope slide. The coated slide was slowly tilted lengthwise (Figure 8B). The water droplet at the high temperature end rolled off at a tilt angle of $\sim 60^\circ$, followed by the droplet at the middle, which rolled off at a tilt angle of $\sim 80^\circ$. The droplet at the low temperature end remained pinned to the surface even at 90° . This result can be explained by a difference in water adhesion strength.

In 2008, Gao's study revealed that the practical work of adhesion is proportional to $1 + \cos\theta_R$,

which means a surface with higher water θ_R has lower water adhesion strength.[37] In 2010, Meuler demonstrated that ice adhesion strength is also proportional to $1 + \cos\theta_R$, suggesting higher water receding CAs give lower ice adhesion strength.[9] Prompted by the different θ_R due to curing temperature, we employed a recently developed test for ice adhesion.[7] Peak removal force (P_s) was determined using a TA Instruments RSAIII by removal of an ice cylinder with a probe fitted to the upper grip at -10°C . Details are available in the cited reference.

As shown in Figure 9, with a $0.05\ \text{mm/s}$ probe speed and $2\ \text{mm}$ probe

distance, P_s is $\sim 420\ \text{kPa}$ for the 25°C cured coating but decreases to $\sim 320\ \text{kPa}$ for the 100°C cured coating. P_s for the 60°C cured coating is intermediate at $\sim 400\ \text{kPa}$. The 25% reduction in

Figure 9. Peak removal force in shear (P_s) as a function of curing temperature of Sylgard 184 coatings with thickness of $15\ \mu\text{m}$.

Figure 10. Peak removal force in shear (P_s) as a function of $1 + \cos\theta_R$ of Sylgard 184 coatings with thickness of $15\ \mu\text{m}$.

the contact angle to decrease. The insolubility of PDMS with the fluorinated moieties causes this self-association into ordered domains as reported earlier.[43, 44]

To mimic the solid state, Dynamic Light Scattering (DLS) on solutions of modifier **2** in low molar mass PDMS revealed, self- aggregation at ~0.4 wt%. The point at which self-aggregation occurs may be considered an upper critical solution temperature (UCST), or the temperature above which the mixture components become miscible, driven by incompatibility of fluororous side chains and the PDMS fluid.

In summary, the above results led to the concept of “more is less” for the SM **2**. A phase transition is responsible for the decrease in the surface concentration of fluororous groups, resulting in the decreased advancing contact angles at modifier concentrations higher than 0.4 wt%. Figure 10 depicts “the more is less” model, showing the increase of aggregate/micelle formation with the increase of modifier concentration.

DCA simultaneously permitted the examination of “leaching” into water and hence potential contamination. Leachates typically reduce the surface tension of water, causing a substantial change in the CAs. Interestingly, there was no detectable contamination of water by the modified PDMS materials during DCA analysis.

Experimental.

Materials. Original publications provide experimental details for preparative procedures and characterization methods.

Contact angles. Prior to

2008 a Cahn instrument was used for DCA measurements (designated “Cahn” in the text and figures). Between 2008 and 2016 a Thermo-Fisher DCA instrument was employed (“Thermo Fisher”). Currently, a First Ten Angstroms DCA-100 is in use (“FTA DCA-100”).

Common to all measurements are immersion-withdrawal rates of 100 $\mu\text{m/s}$. Unless otherwise noted, the time between immersion and emersion (dwell time) is 10 s and the surface area of the vessel containing water was 12 cm^2 . For measurements, a coated glass coverslip hangs from an electrobalance which measures the vertical force, F . The initial mass is tared to zero as the viscous force acting on the sample as it moves in water is negligible.[45]; γ_L for water is 72.8 dynes/cm; the perimeter P of coated slides is 42.5 mm. From these parameters, Eq 1 describes F measured by the electrobalance.

$$F = P \gamma_L \cos \theta - F_b \quad \text{Eq 1}$$

During the DCA experiment, F varies with the buoyancy force F_b , which is proportional to the depth of immersion. The contact angle may be determined by extrapolation to the ordinate at the maximum (or minimum) development of force on immersion or emersion if F_b is assumed to be negligible at this position. Programs on instruments such as the FTA DCA-100 provide an selection of mass, force or contact angle as a function of depth of immersion. For measurements acquired with Cahn instruments, θ_A and θ_R were calculated using the extrapolation procedure noted above and Eq 2.

$$\cos \theta = F/p \gamma_L \quad \text{Eq 2}$$

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Notes

The authors declare no competing financial interest.

Acknowledgement: The authors thanks the National Science Foundation DMR-1206259, Polymers/Biomaterials Programs (DMR-1608022) and the School of Engineering Foundation for support of this research.

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