Attractive forces slow contact formation between deformable bodies underwater

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Edited by Zhigang Suo, Harvard University, Cambridge, MA, and approved August 17, 2021 (received for review March 14, 2021)

Thermodynamics tells us to expect underwater contact between two hydrophilic surfaces to result in stronger adhesion compared to two hydrophobic surfaces. However, the presence of water changes not only energetics but also the dynamic process of reaching a final state, which couples solid deformation and liquid evacuation. These dynamics can create challenges for achieving strong underwater adhesion/friiction, which affects diverse fields including soft robotics, biolocomotion, and tire traction. Closer investigation, requiring sufficiently precise resolution of film evacuation while simultaneously controlling surface wettability, has been lacking. We perform high-resolution in situ frustrated total internal reflection imaging to track underwater contact evolution between soft-elastic hemispheres of varying stiffness and smooth–hard surfaces of varying wettability. Surprisingly, we find the exponential rate of water evacuation from hydrophobic–hydrophobic (adhesive) contact is three orders of magnitude lower than that from hydrophobic–hydrophilic (nonadhesive) contact. The trend of decreasing rate with decreasing wettability of glass sharply changes about a point where thermodynamic adhesion crosses zero, suggesting a transition in mode of evacuation, which is illuminated by three-dimensional spatiotemporal height maps. Adhesive contact is characterized by the early localization of sealed puddles, whereas nonadhesive contact remains smooth, with film-wise evacuation from one central puddle. Measurements with a human thumb and alternatively hydrophobic/hydrophilic glass surface demonstrate practical consequences of the same dynamics: adhesive interactions cause instability in valleys and lead to a state of more trapped water and less intimate solid–solid contact. These findings offer interpretation of patterned texture seen in underwater biolocomotive adaptations as well as insight toward technological implementation.

Significance

Understanding underwater contact mechanics between soft materials and hard surfaces is of prime importance due to its ubiquity and practical relevance. From biological creatures climbing on flooded surfaces and human figures getting grip on wet surfaces to adhesives sealing a wound underwater, performance depends upon water evacuation to achieve contact. We report a counterintuitive relationship between adhesion and water evacuation. Surfaces with stronger thermodynamic work of adhesion show slower evacuation rates as a result of water entrapment in isolated puddles. Interestingly, the evacuation rates speed up at the point of zero underwater work of adhesion. These insights pave the way for developing materials for achieving underwater adhesion/grip and avoiding liquid entrapments via proper combination of chemistry and surface structure.

Author contributions: M.S., N.K., A.D., and H.K. contributed equally to this work. M.S. and N.K. designed research; M.S. and N.K. performed research; M.S., N.K., A.D., and H.K. analyzed data; and N.K. wrote the paper. The authors declare no competing interest.

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This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2104975118/-/DCSupplemental.

Published October 6, 2021.
Several studies have extended the elastohydrodynamic theory to systems in which the soft surface is an elastic film supported by a hard substrate (20–22). There, a significant amount of stress is transferred to the underlying substrate, resulting in a higher effective elastic modulus, and this reduces the elastohydrodynamic response in comparison to that observed for the elastic half-space made of the same material. Frechette et al. measured the deformation and hydrodynamic forces simultaneously to explain the role of elastic forces on hydrodynamic interactions and hence provided insights into the dynamics of contact formation due to the release of stored elastic energy (23). They also disentangled the contribution of elastic compliance and surface roughness to elastohydrodynamic deformation by comparing the measured film thicknesses with those predicted from lubrication theory (15, 20, 24). The advancement in elastohydrodynamic theory has provided a central understanding about the initial state (before any contact) of systems critical to soft coatings for tribology, adhesives, and biomaterials. However, desired end properties such as underwater adhesion or friction between soft–hard contacting pairs require the evacuation of trapped water for intimate solid–solid contact, and this condition is still difficult to comment upon without a detailed understanding of the processes following the initial deformation, especially when long-range, adhesive interactions are not negligible.

Here, we report the evolution of underwater contact between soft elastomeric lens and hard surface of variable surface energy by visualizing the initial contact formation and measuring the evolution of the entrapped liquid film over time. We determine the dependence of fluid evacuation on the surface wettability and elastomer modulus in the underwater collision, as it is essential to any observed transient and final adhesion and friction state. Our results have implications for problems in which the timescale of wet contact is relevant: from tire traction on wet roads to design of underwater adhesives and lubricants to understanding biological solutions for wet traction and adhesion.

**Principles of Experiment**

Three-dimensional (3D) imaging of the contact made between a soft elastomer and hard substrate underwater was achieved using the principle of frustrated total internal reflection (FTIR) (details in Methods). Fig. 1A shows a sketch of the experimental setup. A BK7 glass (refractive index $\mu = 1.51$) prism has the top surface enclosed in a polytetrafluoroethylene chamber filled with water ($\mu = 1.33$). The polydimethylsiloxane (PDMS, $\mu = 1.43$) was selected as an elastomer because of several reasons. The PDMS has a negligible swelling ratio in water, which ensures constant material properties and reduces the possibility of absorption of any water throughout the observed process (25). The PDMS elastomeric network is fully crosslinked and does not contain any nanoparticles for reinforcement. Additionally, the PDMS lenses (blue hemisphere in Fig. 1A) used were all Soxhlet extracted (details in SI Appendix, section 1) for 3 d before use to ensure the removal of uncrosslinked chains, which can potentially change the viscosity and wetting of entrapped water, hence the evacuation dynamics. The PDMS lens is brought into contact with glass substrate with a translational Z-stage connected to a stepper motor at a constant approach velocity sufficient to cause elastohydrodynamic deformation of the elastomer (0.9 mm/s). Images are captured by high-speed camera at different frame rates based on the timespan of the process studied. Fig. 1B shows the schematic of phenomena at contact interface before the contact between an elastomer and a hard surface. The hydrodynamic resistance causes the elastic deformation to the elastomer and surface forces might play a role in evacuation of liquid when the two surfaces are in close proximities.

We explored the parameter space encompassing three moduli (0.7, 1.5, and 9.7 MPa) for soft PDMS lens and six substrates with water contact angle in air ranging from 0 to 108°. The PDMS lenses of variable elastic modulus were synthesized by employing network theory (details in SI Appendix, section 1) (26). Evolution of contact area of the lenses while pressed against a low–surface energy (~24 mJ/m$^2$) monolayer (octadecyltrichlorosilane [OTS]-treated silicon wafer) was analyzed to extract the modulus using the Johnson–Kendall–Roberts (JKR) model (details in SI Appendix, section 2). To prepare substrates with varying contact angles, an OTS monolayer was solution deposited on glass prism following the procedure described in the literature (3). The static water contact angle on OTS-t-glass prism is measured as 108° ± 3° (three repeats at different spots). Lower contact angles (87.7° ± 0.3°, 51.2° ± 1.8°, 35.9° ± 1°.0, 25.4° ± 0.8°, and 0° ± 0°) were achieved by plasma treating the OTS-t-glass prism for different exposure times. The methodology for surface preparation (SI Appendix, section 1) and resulting surface chemistry (evaluated by X-ray photoelectron spectroscopy and attenuated total internal reflection spectroscopy) has been described in great details elsewhere (3).

Fig. 1C shows the transformed FTIR image (at $t = 1.5$ s) for PDMS/intermediate wettability glass (with water contact angle of $51° ± 1.8°$) contact underwater. The dark region represents the pixels for which the evanescent wave is totally frustrated due to contact of PDMS with the substrate, resulting in refraction of incident light into PDMS, whereas the white region represents pixels where the wave is partially frustrated due to presence of entrapped water. The captured image is elliptical due to optical light path and back transformed (Fig. 1 C, Left) using aspect ratio of ellipse (calculation in Methods) to perform analysis. A look-up table (SI Appendix, Fig. S2) between the modulus of total reflectivity squared (reflectance) versus film thickness was prepared (procedure in Methods) using the Stokes’ relations and Fresnel equations for p-polarization, which was then used to convert the reflectance of every pixel to the height of water entrapped (27). Any pixel with water film thickness less than 3 nm is considered as contact due to limit in resolution for this technique. Furthermore, Fig. 1C shows the side view of the height map corresponding to the grayscale image. The obtained spatiotemporal (height maps at each time step) data are used for calculating the volume of entrapped water by integrating the height maps at each timestep, represented in Fig. 1D.

**Results**

**Water Evacuation Dynamics.** Fig. 1D shows the water evacuation profiles for two extreme cases of wettability (i.e., PDMS/glass and PDMS/OTS-t-glass contact underwater). The volume of entrapped water was observed to decrease exponentially with time after initial contact, irrespective of the substrate chemistry and the PDMS elastic modulus (G). The decay constants (K) for different cases were obtained by fitting the volume versus time data to equation, $V(t) = V_0 e^{-Kt}$, and the results are shown in Fig. 2. In Fig. 1D, it can be noted that the time required to evacuate water from a hydrophobic–hydrophobic entrapment is ~3 orders of magnitude higher than that required for the hydrophilic–hydrophobic entrapment. The results are surprising, as we expected that the water evacuation would be faster from two hydrophobic surfaces entrapment due to their thermodynamic inclination to be in contact. We expect the contact between two hydrophobic surfaces underwater to be dry based on earlier measurements using surface-sensitive sum frequency generation spectroscopy (SFG) and the measured work of adhesion (~80 mJ/m$^2$, same as thermodynamic prediction) between PDMS/OTS-t-glass underwater. In comparison, we expect the glass–hydrophobic contact should always contain a thin layer of water, which has also been verified by SFG (3).

**Effect of PDMS Modulus and Substrate Wettability on Rate Constant.** In Fig. 2A, we plot the decay rates (K) for water evacuation as a function of bulk modulus (G) of PDMS for substrates with different wettability represented by water contact angles.

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The positive slope for all the trends represents faster evacuation for higher G. Furthermore, the value of K increases with a decrease in substrate contact angle. It is evident from the graph that the effect of modulus (less than 1 order) is very small compared to that of surface wettability (more than 3 orders) for the parameter range explored here. Fig. 2B shows a plot of log(K) versus contact angles for PDMS lenses with different modulus. There is a notable, apparent change in slope around ~42° contact angle (intersection of the two linear fits) for all the cases of G, indicating a transition in the mode of evacuation dynamics. The transition is also clearly visible in a log(K) versus cosine of contact angle plot (SI Appendix, Fig. S4). We were unable to increase the modulus of PDMS any further due to limitations in synthesis, and the use of other stiffer polymers would reduce the elastohydrodynamic deformation (by 2 to 3 orders of magnitude for glassy polymers) and would make it difficult to monitor using FTIR (21, 28). For one hydrophobic surface, we explored the effect of loading velocity on initial volume entrapped (after the complete approach) and on the rate constant for a particular surface chemistry. While initial volume increases with loading velocity, this leads to no observable change in K (SI Appendix, Fig. S5).

**Initial Contact Formation and Modes of Evacuation.** To shed more light on the changes in the evacuation rates, Fig. 3 (and Videos S1–S3) shows the spatiotemporal height maps for initial contact formation and the following water evacuation for interfaces between PDMS lens (0.7 MPa) and three different substrates [glass (0°), intermediate glass (i-glass) contact angle (35.9° ± 1.0), OTS-t-glass (108° ± 3°)]. Corresponding grayscale images are shown under each height map. t = 0 is chosen arbitrarily from initial frames of each of the three cases where the elastohydrodynamic deformation can be noticed clearly.

Fig. 3A shows the entrapment of water in bell shape (t = 0) and the subsequent growth of area (t = 0.14 s) outside the bell as the normal displacement progressed to reach to the final normal load for the PDMS lens/glass contact underwater. A continuous thin film of water is observed throughout the apparent contact area with the additional symmetric puddle (water bell) in central position (Fig. 3A and SI Appendix, Fig. S6). The puddle height decreases with an increase in puddle radius (t = 0.140 to t = 3.490 s). Additionally, the 2D line height maps (SI Appendix, Fig. S6) for the contact formation shows the gradual height decrease of thin film and the puddle without any contact between the PDMS and glass, suggesting that the water evacuates axisymetrically without any barrier in flow path. Even though the final state (t = ∞) of the contact interface seems to be completely dry, certainty of intimate atomic contact cannot be guaranteed due to limitation in the film thickness resolution (~3 nm) of the FTIR technique. Previously, the SFG (3) results have shown that the contact interface between hydrophobic PDMS and hydrophilic sapphire surfaces are not dry. Molecular dynamics simulations have also shown that a hydrophobic surface (contact angle > 90°) is fully hydrated even if the second contacting surface is not highly polar (contact angle < 60°). Similarly, the PDMS (hydrophobic) and glass (highly polar) contact is hindered due to the presence of a stable continuous nanometer-thick film of water in between (29). Fig. 3 C, Left shows the initial (t = 0) water entrapment for the PDMS lens approaching OTS-t-glass underwater. Suddenly after the small puddle formation, the puddle gets asymmetrically deformed (as evident in t = 0.014 s). In fact, it is apparent from 2D cross-sections of Fig. 3C (line height maps, SI Appendix, Fig. S6) that the symmetry of the deformed lens is broken (instability) when the peripheral gap thickness is still ~100 nm (for the case with softest lens) and, immediately after, a part of the peripheral bell appears to snap into contact. This leads to enhanced asymmetry (SI Appendix, Fig. S6) and breakdown of the puddle into multiple smaller puddles (t = 0.107 s). Furthermore, it is evident from the 2D line height maps (SI Appendix, Fig. S6) that the majority of the apparent area is true contact (in FTIR limit) between the PDMS and OTS-t-glass at the motor stop time.
and nearby film disappearing \((t = 1.458 \text{ s})\). Similar behavior of increment in the height of puddles is also observed in the PDMS lens/OTS-i-glass interface case, but the process there is much faster and completed even before the motor stop. The evacuation from the smaller puddles at PDMS lens/i-glass interface optically followed the mechanism of that for PDMS lens/OTS-t-glass interface, where the heights of the puddles are found to decrease with time without presence of a continuous thin film. Despite the similarity in the evacuation mechanism, the dynamics of evacuation from PDMS lens/i-glass interface is much faster than that of PDMS lens/OTS-t-glass interface (Figs. 2 and 3), which further emphasizes the role of adhesion in evacuation mechanism.

**Human Thumb Contacts.** To explore the generality of the observations to realistic contacts, we study the dynamics of biological underwater contacts of human digit (thumb outermost layer: stratum corneum) with hard hydrophilic (bare glass) and hydrophobic substrates (OTS-t-glass) in Fig. 4 (larger area with corresponding grayscale images in *SI Appendix*, Fig. S7 and Videos S4 and S5). For both the contacts, it is observed (*SI Appendix, Fig. S7*) that the protruding ridges of the thumb tend to come in contact \((t = 0)\) with the hard substrate in an unconnected fashion. Furthermore, the contact region evolves underwater in two-step coalescence process (from \(t = 0\) to \(t = 0.04 \text{ s}\) and \(t = 0.04 \text{ onwards}\)) similar to that reported earlier for the dry human figure-tip/glass contact \((30)\). The number of junction points increases, (first step, \(t = 0 \text{ to } t = 0.04 \text{ s}\) followed by the growth in their areas (second step, \(t = 0.04 \text{ onwards}\)) resulting in the connection of those junction points into continuous ridges (result of second step). The growth is usually fast (within few seconds) and ascribed to the plasticization (reducing the elastic modulus to few MPa from \(\sim 1 \text{ GPa}\)) of stratum corneum due to hydration \((31, 32)\).

Fig. 4 illustrates the evolution of water heights in a randomly selected region (for evolution of complete region, see *SI Appendix, Fig. S7*) of thumb/glass and thumb/OTS-t-glass contact. It is clear from these spatiotemporal height maps that the thumb valleys act as channels for collection of water from the ridges \((t = 0.10 \text{ s})\), facilitating the growth in contact area. After ridges connect \((t = 0.40 \text{ s})\), for the case of thumb/glass interface (Fig. 4 A, *Top*), we observe that the water valleys are continuous and gradually narrowed with time, enhancing the width of ridges and hence the contact area. Eventually, some of the ridges joined due to the diminishing valleys for some regions of the thumb \((t = 10 \text{ s})\), suggesting evacuation of water through valleys to large extent. In the case of thumb/OTS-t-glass interface (Fig. 4 A, *Bottom*), we observe an instability \((t = 5 \text{ s})\) in the valley region following the ridges connection \((t = 0.40 \text{ s})\) and subsequent water evacuation. There is a sudden breakdown in the continuity of flow path of the valleys, resulting in unconnected entrapments of water in valleys \((t = 5 \text{ s})\), causing evacuation of water to a lesser extent. The long-time dynamics show that the evacuation from these entrapments happen as discreet puddle-wise events (Video S5). To quantify the dynamics of water evacuation, we plot average volume versus time curves for the thumb/glass and thumb/OTS-t-glass contact in Fig. 4B. Initially the water evacuation for both the cases follow similar dynamics with deviations starting at \(\sim 7 \text{ s}\). Interestingly, the asymptotic volume after the evacuation process is much higher for the case of thumb/OTS-t-glass contact. To check for the test subject variability, we have reported the spatiotemporal height maps for another subject in *SI Appendix, Fig. S8* which shows similar features as reported in Fig. 4B.

**Discussion**

Here, we seek to understand the trends in dynamics of water evacuation (Fig. 2) and provide deeper insights into the process of contact formation, subsequent evacuation (Figs. 3 and 4), and their links with the observed rate constants \((K)\). Fig. 2 demarcates the role of PDMS modulus and surface wettability in the

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**Image Descriptions**

Fig. 2. (*A*) Dependence of water evacuation rate constant on elastomer modulus \((G)\) for different substrate wettability represented by the log-log plot. The vertical and horizontal dashed black line segments demarcate the role of substrate chemistry and modulus by comparing the change in order of magnitude in \(K\) values. (*B*) Log\((K)\) versus contact angle plots for three moduli of PDMS. The plots clearly point toward a transition in evacuation dynamics as the slope of data changes \(42° \) [i.e., the point at which underwater thermodynamic work of adhesion is zero (dashed vertical black line)]. The dashed vertical black line segments demarcate the role of PDMS modulus and surface wettability in the transition point for three moduli of lenses. All the rate constants are calculated from the volume entrapped versus time data as shown in Fig. 12.

Fig. 3 C, *Right* illustrates the water evacuation from the small puddles entrapped between PDMS lens and OTS-t-glass contact, where the height of individual puddles goes down with a decrease in puddle radius, in contrast with that of the PDMS/glass contact. In this case, no continuous thin film for the apparent contact is observed, suggesting barriers in the water flow path.

Fig. 3B shows the initial contact formation (*Left*) and the water evacuation (*Right*) from the PDMS lens/i-glass interface. The initial behavior of the system is similar to the PDMS/glass interface, where first we observe water entrapment \((t = 0)\) in a bell-shape due to elastohydrodynamic deformation followed by a decrease in puddle height and an increase in puddle radius \((t = 0.095 \text{ s})\). With the reduction in puddle height, we start to observe an instability and waviness in the puddle film thickness, with water entrapped in a combination of puddles and thin film at the center region \((t = 0.410 \text{ s})\). We then observe the entrapped water in combined (puddle-film) state \((t = 0.410 \text{ s})\) further coalescing with existing puddles growing
observed evacuation dynamics. The faster dynamics for higher G could be due to lower apparent contact area at same normal force, hence, a smaller water evacuation path. Another possibility is that the lenses with higher G cannot conform to the surface roughness, which can result in wider channels for water evacuation. The significant effect of surface wettability on evacuation dynamics and the change in slope in log(K) versus water contact angle (θ) around ∼42° has been rationalized using a thermodynamic argument in the Transition in Evacuation Dynamics section.

**Transition in Evacuation Dynamics.** The crossover in slopes (Fig. 2B) of rate constants is intriguing, as it points toward a transition in the evacuation mechanism. The significance of the transition point with respect to substrate wettabillity can be related to the corresponding adhesion energies for the system using the Young (33) and Dupré (34) equations and available experimental values.

The Dupré equation for two continuum media (Sub1 and Sub2) interacting in a third medium (say underwater) can be written as Eq. 1.

\[
(W_{Sub1-Sub2})_{Water} = \gamma_{Sub1-Water} + \gamma_{Sub2-Water} - \gamma_{Sub1-Sub2} \]  

where \((W_{Sub1-Sub2})_{Water}\) is the thermodynamic work of adhesion underwater, and \(\gamma\)'s are interfacial energies between Sub1, Sub2, and water. Subtracting from Eq. 1 the Dupré expression for Sub1-Sub2 in air (third medium) and substituting the difference in interfacial energies underwater and in dry case for Sub1 and Sub2 in terms of water contact angles (\(\theta_{Sub1-water}\)air and \(\theta_{Sub2-water}\)air) and water interfacial energy (\(\gamma_{Water}\)) using Young’s equation we get, Eq. 2.

\[
(W_{Sub1-Sub2})_{Water} = (W_{Sub1-Sub2})_{Air} - \gamma_{Water} \cos(\theta_{Sub1-water})_{air} + \cos(\theta_{Sub2-water})_{air} \]

\[\text{[2]}\]

For this study, Sub1 is hard substrate (Sub), and Sub2 is PDMS. Plugging in the interfacial energy for water–air interface (72.8 mJ/m²) and the contact angle (110°) of water on PDMS in Eq. 2, we get Eq. 3.

\[
(W_{Sub-PDMS})_{Water} = (W_{Sub-PDMS})_{Air} - \gamma_{Water} \cos\theta_{Sub-water} + 25 \]

\[\text{[3]}\]

Assuming that the observed transition point (∼42°) represents the point where \((W_{Sub-PDMS})_{Water}\) is equal to 0, we estimate the \((W_{Sub-PDMS})_{Air}\) to be equal to 29 mJ/m². The estimated dry work of adhesion for ∼42° water contact angle is in agreement with the experimental value (30 ± 3 mJ/m²) measured during the loading cycle using the JKR method (3). The change in slope where the underwater thermodynamic work of adhesion is zero suggests that formation of dry contacts or barriers in water flow path is responsible for slowing down the evacuation rates, as seen in Figs. 1D and 2. The connected barriers in flow path presents the argument of sealing mechanism or water entrapment in smaller puddles.

We highlight that the observed transition point (∼42°) of transition in dynamics should not be considered as a special number. The transition point depends upon the thermodynamics of the three phases. Any change in the surface energy of the elastomer or selected liquid will shift the transition point to either the lower or higher side. The open question is to synthesize the elastomers with varying surface energies and hence design a universal evacuation curve. Furthermore, modeling the dynamics about the transition point requires a broad consideration of parameter space.
which is yet to be discovered, especially the influence of roughness holds our attention and will thrive in the field of underwater contact mechanics.

Contact Formation and Subsequent Evacuation. Uniting our observed trend (Figs. 1D, 2, and 3) with the established knowledge of thermodynamics and material deformation allows us to explain the contact formation in terms of two sequential processes. First, for all the cases presented in Fig. 3, the PDMS lenses undergo elastohydrodynamic deformation due to liquid viscous forces, which results in entrapment of water (confirmed from the height maps before contact; SI Appendix, Fig. S6). The contact region has water trapped in the center as a bell-shaped cavity, with contact initiating at the periphery. The shape of this initial cavity is generic (also observed for much stiffer, glassy solids and more-viscous fluids), though its scale depends simply on competition between respective factors of solid and liquid response: lens curvature and modulus versus collision speed and liquid viscosity (21, 28). The second process differs depending on the surface energy of the substrate. For the case of PDMS/glass contact, the water evacuates rapidly and smoothly through a thin film of water, reducing its height with time (Fig. 3A). In the case of PDMS/OTS-t-glass contact, the puddle quickly and asymmetrically breaks into smaller puddles, which drain over a much longer period (Fig. 3C), limited by a tighter seal of the adhesive contact at the periphery. The possibility that absorption of a portion of the entrapped water into the PDMS lenses plays a parallel role with lateral drainage is not apparent in the data and would not explain the transition in the rates with surface chemistry, as the same lenses are used in all experiments and the only variable is the surface chemistry of the glass.

Now, we discuss the similarities in the water evacuation dynamics for model system (PDMS lens/hard contact) with a complex reality (human thumb/hard contact). The water evacuation dynamics for both thumb/glass and thumb/OTS-t-glass contact is identical until ∼7 s (Fig. 4B) and can be ascribed to the presence of valleys, which facilitate the drainage (Fig. 4A and SI Appendix, Fig. S7). We observe striking differences between the dynamics of thumb/glass and thumb/OTS-t-glass contact after ∼7 s that can be explained with our knowledge of evacuation process for the model systems. The cleaned surface of stratum corneum is known to be highly hydrophobic (contact angle of 125 to 130°) (35), due to which the thumb/OTS-t-glass interface should behave in a similar fashion as PDMS lens/OTS-t-glass interface at microscopic scale. For initial region (until ∼7 s) the elastic modulus is high enough such that the adhesive forces have no effect on the dynamics. Subsequently, we observe sudden asymmetric break down of the valleys (Fig. 4A, Bottom) for the case of thumb/OTS-t-glass in which the thumb/OTS-t-glass interface reaches to localize the valleys which facilitate the drainage of water. The instabilities in the valleys for thumb/OTS-t-glass contact are similar to the breakdown of a large puddle into multiple smaller puddles for the case of PDMS lens/OTS-t-glass contact. Additionally, we observe asymptotic volume for both thumb/glass and thumb/OTS-t-glass contact. This volume represents static condition in the
observation timescale, wherein the elastic stiffness of the ridges in the fingerprint support cavities of water in the valleys between. The previously reported drop in stiffness of the stratum corneum of a human finger with hydration/moisturization is likely changing this elastically supported volume as the contact evolves. The larger value of static volume of trapped water associated with thumb/OTS-t-glass contact is consistent with the notion that sealed puddles of incompressible water are contributing to the resistance of the fingerprint ridges to further collapse.

Here, we would like to point out that for the hydrophobic–hydrophobic (PDMS lens/OTS-t-glass) contact formation under water (Fig. 3C), we have made intriguing observations which are discussed in the next two sections.

Water Puddle Breaks Down before Contact, an Instability for Hydrophobic–Hydrophobic Entrapment. The instability in the deformation of a single puddle for the case of PDMS lens approaching OTS-t-glass before any direct contact (Fig. 3C and SI Appendix, Fig. S6B) points toward the presence of long-range hydrophobic forces, popularly known as solvation forces. When two hydrophobic surfaces approach each other underwater, a water vapor cavity formation takes place that applies negative Laplace pressure on both the surfaces, resulting in the observed attraction between them (36). The cavity formed is a transient state, which is lower in energy than the two hydrophobic surfaces separated by some water layer but is still higher in energy when compared to the final thermodynamic equilibrium state of direct solid contact (36, 37). These hydrophobic solvation forces cannot be accounted for by the Derjaguin–Landau–Vervey–Overbeek or Lifshitz theory and has now been proven to exist experimentally as well as through simulations and theory (29, 36, 37). Using surface force apparatus, it has been shown that these forces start to show up at separations of 20 to 100 nm (depending upon the hydrophobicity) for two rigid hydrophobic surfaces underwater (36, 37).

We also observe that during instability, only a part of periphery contact with the substrate (SI Appendix, Fig. S6B). We speculate that as the water evacuation rates are high initially due to the high stored elastic energy, hence hydrostatic pressure, the peripheral edge opposite to the edge in contact is found to stay out of contact for some time to facilitate water evacuation. After a certain time, the entire peripheral area is found to seal with the smaller water puddles trapped in between. The evacuation mechanism for these smaller puddles following the sealing is unobservable and has been hypothesized in the next section.

How is Water Escaping from Sealed Hydrophobic–Hydrophobic Entrapment? The water evacuation from the smaller puddles entrapped between the PDMS lens and OTS-t-glass (Fig. 3C) can happen in multiple ways. PDMS elastomer, despite its negligible absorption of water (∼40 mol/m³), is known to allow some diffusion through its bulk in response to concentration gradients inside and across its surfaces (38). In our case, presoaking the PDMS lens for ∼6 h prior to data collection and conducting measurements underwater were found to eliminate its effect, as no differences in the decay constant (K) were observed upon increasing the presoaking time or across successive collisions in subsequent hours of the experiment. Furthermore, the difference in the rate constants for evacuation (K values reported in Fig. 2) for the glass substrate with 88° and 108° contact angle does not support the diffusion argument as both the substrates make adhesive contact with PDMS underwater, and the K values should be similar if the mode of evacuation is diffusion through the PDMS material. Lastly, it is possible that the water is evacuating out along the interface through gaps smaller than the measurable length scale. It is well known that even though all the glass surfaces used are optically smooth, these surfaces are rough at nm-length scale (3). The roughness at smaller-length scales can remain as an interconnected channel, facilitating the water evacuation along the interface (15). Furthermore, the final equilibrium state can have majorly dry regions with water sealed at small-scale roughness. The effect of surface roughness on water evacuation is difficult to investigate using the FTIR technique, as the rougher surfaces will contribute to the light scattering and make the data analysis impractical (27). On the other hand, making rough or patterned PDMS structures are totally feasible and will be the scope of our future studies.

Conclusion

Competition between adhesive forces and fluid drainage can play a crucial role in collisions between deformable objects (28). While adhesion energetically favors contact between hydrophobic contacting pairs, that very affinity dynamically leads to entrapment of isolated puddles, thus delaying their ultimate contact. The paradoxical relationship between kinetics and thermodynamics may explain why underwater adhesive designs which rely on surface hydrophobicity alone do not produce the best performance. Patterned or special morphology is necessary to increase evacuation rates (12).

We have demonstrated that increasing adhesive interaction between soft bodies leads to as many as 3 orders of magnitude in dynamics inhibition of their contact formation due to tighter sealing of trapped water in a controlled system with simple geometry. In the complex practically important system—human thumb contact underwater—we found that competition between the same physical drivers plus surface texture lead to a logically consistent, nontrivial result: the surface texture facilitates the initial drainage until the point where the adhesive forces overcome the elastic response of the thumb, which prevents longer-term approach to more fully intimate contact due to better sealing of puddles trapped between the adhesive contact.

Achieving conformality in wet/unwater environments is an inevitable requirement for most of the tissue adhesives and hemostatic sealants. The rapid yet robust performance of any bioadhesive confronts the challenge of water removal (39, 40). Furthermore, evolution of underwater contact area is important, as it determines the creation of friction which is essential in everyday life. It would have been impossible to even hold a wet glass of water without any intimate contact. Though the increase in real contact area at microscopic level to high tangential frictional force in dry haptics has been well studied, the augmentation of human tactile sensing underwater is challenging, as the primary factors include the length scale and time scale of contact (30, 41). Quantifying the area growth laws and exploring the wet haptics will be scope of our future studies. Additionally, the fundamental insights stemming from this study will act as critical design parameters and further development of the field of tissue adhesives.

Methods

In Situ Contact Experiments and Analysis. FTIR setup and experiments. Schematic of the FTIR setup is shown in Fig. 1A. The top surface of the dove prism is illuminated by a polarized mounted light-emitting diode (LED) (M660L4, λ = 665 nm, bandwidth 20 nm; obtained from Thorlabs). The dove prism glass material is transparent to the light wavelength, and the prism surface is optically flat. Incident angle (θi = 64.4° ± 0.1°) with respect to glass surface normal of the p-polarized light (λ = 665 nm) has been selected between the critical angle for glass/water and glass/PDMS interface. At FTIR condition, an evanescent wave propagates along the interface, with its intensity decaying as an exponential function along the Z direction in the second medium. When a third medium comes into evanescent wave, a portion of the energy is refracted in third medium. This energy loss carries the information of film thickness of the second medium. Initial quantitative model (42, 43) for film thickness assumed a simple truncation of evanescent wave intensity, whereas later (27) it was proved that multiple transmissions and reflections and also the light polarization plays a crucial role in accurate predictions of film thickness. Thus, a polarizer was used in the light
path to set the p-polarization of the incident light. When a PDMS lens approaches the glass prism underwater, the FTIR phenomenon starts to occur at a scale comparable to the wavelength of light. The Z-stage is connected to PDMS lens through a load cell to control the vertical displacement of the lens to achieve an initial load of \((7 \pm 0.2)\) g, after which the motor is stopped.

**Data acquisition and image processing.** The reflected intensity profiles from the internal face of the dove prism were collected using a high-speed camera (VECO410 procured from Phantom) with a video resolution of 128 x 128 pixels at 24 and 1,000 fps. The fast frame rate (1,000 frames/second [fps]) was good enough to visualize the initial contact formation, whereas the slow frame rate (24 fps) allowed us to capture long time videos for studying water evacuation dynamics from the hydrophobic–hydrophobic entrapment. Fig. 18 (Left) shows a raw grayscale frame of a video which shows both the region of dry contact or dark pixels (i.e., PDMS in contact with the hard substrate) as well as the bright pixels, which correspond to the case of thin water film in between the PDMS and substrate. Before performing the experiments, a water droplet is put on the top of a dry hydrophobic prism, which gives a perfectly circular boundary for glass/water, water/PDMS, and PDMS/water interface. The captured image is elaborated. The data for second subject is presented in SI Appendix, Fig. S2 to render a 3D height map. The look-up was created using the relationship between normalized reflection intensity (reflectance, \(p^2\)) and the film thickness. This reflectance equation (Eq. 6) accounts for multiple reflections and transmissions (geometric series) using Stoke's relations and for light polarization through Fresnel equation and has been reported in great detail elsewhere (27, 44). The lateral resolution of the camera is \(\sim 15\) \(\mu\)m/pixel. To verify the FTIR technique and our analysis protocol, we measure (SI Appendix, Fig. S3) the air film thickness between a convex glass lens (radius of curvature: 386 mm, obtained for Thorlabs) and glass prisms (pristine and OTS coated) under a 20-g load. The measured gap thicknesses showed an excellent agreement with the Hertzian contact theory.

The total reflected amplitude \((p)\) is related to indices of refraction of glass \((n_G)\), water \((n_L)\), and PDMS \((n_M)\). \(\theta_i\) and \(\theta_f\) denote the incident angles for glass/water, water/PDMS, and PDMS/water interface. \(j\) is an imaginary number, and \(h\) is the gap or water film thickness between prism and PDMS lens.

**Human thumb experiments.** Right thumb of two subjects (first authors, both male, right-handed Asian) were brought into contact at an angle of \(0^\circ\) with glass prism. The glass was loaded to a constant force of \(10 \pm 0.5\) N (force sensor installed at the bottom of the glass prism in Fig 1) and was held in position for 1 min. Three repeats were done for both the subjects. For every repeat, 15 nonoverlapping areas \((4 \times 4\text{ mm})\) were averaged for volume, and one of the repeats for one of the subjects is shown as a function of time in Fig. 44 for clarity. The data for second subject is presented in SI Appendix, Fig. S8. For both the cases, \(t = 0\) s is defined as the time when FTIR technique starts to sense the thumb ridges. The apparent area of thumb stops changing at \(t = 0.1\) s. Before the experiment, the thumb of the subject was first washed with commercial soap, then wiped with ethanol using a nonwoven paper, and finally rinsed with ultrapure water (Millipore filtration system, volume resistivity of 18.2 M\(\Omega\)cm) for 10 s. This study was deemed exempt from the Institutional Review Board (IRB) and approved by The University of Akron.

**Data Availability.** All study data are included in the article and/or supporting information. Additional data related to this paper is available at https://zenodo.org/record/5518167 (45).
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