A Bioinspired Wet/Dry Microfluidic Adhesive for Aqueous Environments

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A pressure-sensitive, nonreacting and nonfouling adhesive which can perform well both in air and underwater is very desirable because of its potential applications in various settings such as biomedical, marine, and automobile. Taking a clue from nature that many natural adhesive pads have complex structures underneath the outer adhesive layer, we have prepared thin elastic adhesive films with subsurface microstructures using PDMS (poly(dimethylsiloxane)) and investigated their performance underwater. The presence of embedded structure enhances the energy of adhesion considerably both in air and underwater. Furthermore, filling the channels with liquid of suitable surface tension modifies the internal stress profile, resulting into significant enhancement in adhesive performance. As this increase in adhesion is mediated by mechanics and not by surface chemistry, the presence of water does not alter its performance much. For the same reason, this adhesion mechanism works with both hydrophobic and hydrophilic surfaces. The adhesive can be reused because of its elastic surface. Moreover, unlike many other present-day adhesives, its performance does not decrease with time.

Introduction

Underwater or wet adhesion poses a significant challenge for the performance of pressure-sensitive adhesives because of the propensity of water to loosen adhesion and difficulty in dispelling water molecules, especially from the hydrophobic surfaces. The presence of water not only weakens the intersurface physical adhesive forces such as the van der Waals and acid–base interactions but may also alter chemical bonds. Adhesive joints that need to withstand a wet environment created by moisture, rain, underwater applications, and body fluids are common in marine applications, outdoor structures, automobiles, biomedical and dentine prosthetics, medicinal and surgical tapes, and patches in biomedical applications.

The most widely used strategies for effective wet adhesion are using either synthetic reactive glues like cyanoacrylate or bioderived glues like fibrin. However, the recent trend in material research demonstrates the potential of bioinspired underwater adhesives like gecko and beetle inspired microtexturing of the surface or glues inspired by marine bioadhesives such as mussel proteins or sometimes using both in combination. We demonstrate here a novel microstructured adhesive which is equally effective in both dry and wet environments as well as in adhesion to both hydrophobic and hydrophilic surfaces. The adhesive consists of a smooth, nearly elastic layer in which several subsurface microchannels are buried with or without a capillary liquid. This “microfluidic” adhesive was found to give a strong adhesion in air because of its crack arrest properties and the compressive stresses engendered by the capillary liquid. Further, such an adhesive is reusable and nonfouling because of its smooth and elastic surface, unlike the pressure-sensitive adhesives that undergo cohesive failure and employ viscoelastic surfaces to increase the work of adhesion by viscous dissipation. Adhesive pads found at the feet of different insects like Tettigonia viridissima (commonly known as grasshoppers) and Rhodnius prolixus and vertebrates like tree frog show complex subsurface structure. Inspired by this observation, our microfluidic adhesive mimics the underlying physics with a comparatively simpler geometry. In this present study, we show that the microfluidic adhesive is in fact equally effective in a wet environment because such a “structural” adhesive harnesses thermodynamic factors other than the surface chemistry or the kinetic factors such as viscoelasticity to modulate its energy of adhesion. In this glueless adhesive process described here, neither the surface topography nor the surface chemical properties (covalent bonding, etc.) are altered so as to produce a reversible and reusable adhesive that is much stronger vis-à-vis an elastic nonstructured layer. In some biomedical applications, such a strategy could also avoid complications of irreversible adhesion, contamination, inflammatory, thromboembolic and septic complications.
toxicity, and the possibility of viral transmissions from the glues derived from biosources.\textsuperscript{4,5,20}

**Experimental Section**

**Materials.** Elastic model adhesive for this work was made by cross-linking liquid poly(dimethylsiloxane) (PDMS) (Sylgard 184, Dow Corning product) on a cleaned rigid laboratory glass slide as substrate. For making smooth films, PDMS precursor liquid mixed with the curing agent (10:1 by weight) was cast between two glass plates; one plasma-cleaned and one silanized. Spacers were used to make PDMS films of specified thickness. After cross-linking, the silanized plate was peeled away to leave a smooth solid film rigidly bonded to the plasma-cleaned glass plate. To make film with embedded channels, the templates using slender steel rods (surgical needles) of diameters 710 μm were used.\textsuperscript{15,16} The templates were first placed on a plasma cleaned glass plate on which PDMS precursor liquid was poured. After curing the PDMS at 100 °C for ~2 h, the needles were removed from the film to obtain an elastic adhesive film with embedded cylindrical channels inside the adhesive. Silicone oil of viscosity 380 cP and surface tension ~22 mJ/m\(^2\) was used for filling the channels in the adhesive layer. This particular viscosity was chosen because in our earlier study of adhesion in air, a viscosity range of 100–1000 cP was found to be the most effective for enhancing adhesion.\textsuperscript{15} Microscope coverslips coated with a self-assembled monolayer (SAM) of octadecyltrichlorosilane molecules were used as the hydrophobic contactors. For hydrophilic contactor, the microscope coverslips were cleaned in a piranha solution (30 vol % / 70 vol % H\(_2\)O\(_2\) and 98% H\(_2\)SO\(_4\) solution) for about 30 min. After that, they were thoroughly cleaned with deionized water to remove any trace of acid and then blow-dried with dry N\(_2\) gas. To alter the hydrophobicity of the contactor, the contactor was coated with self-assembled monolayer of silane molecules of various chain length and alkyl groups like hexadecyltrichlorosilane, undecyltrichlorosilane, butyltrichlorosilane, and methacryloxypropyltrimethoxysilane.

**Experiment.** We measured the energy of adhesion of our adhesive using a peel test method, as shown in the schematic of Figure 1a. We first fixed the substrate, to which the adhesive was strongly attached, to a Petri dish using double-sided tape to prevent any movement of the substrate or the adhesive. A microscope coverslip with silane monolayer coating was then brought in full contact with the adhesive film immediately after filling up the channels before the capillary stresses caused the formation of surface bumps. In some cases, surface was allowed to relax and form the equilibrium bumps. A full contact with the adhesive film was then established by eliminating the bumps by pressing. The capillary stress could thus be fully regenerated as evidenced by the fact that both the procedures of adhesion pressing. The capillary stress could thus be fully regenerated as evidenced by the fact that both the procedures of adhesion

filled with deionized water. To prevent water evaporation, the Petri dish was covered with a lid having a small opening to allow the lifting arrangement to go in. The level of water was kept at least 1 cm above the top surface of adhesive film. All the experiments in air were done in ambient condition at 60–80% relative humidity. We found that making adhesion underwater by dispensing water completely from the space between the contactor and the adhesive film to engender full contact was difficult, especially with a hydrophilic contactor. In such cases, contactor was first brought in contact in air, and then the whole assembly was immersed in water. When the contacting surface was made hydrophobic, an intimate contact without trapped defects could also be obtained underwater.

**Results and Discussion**

Figure 1b summarizes the results of typical peel tests done in air (curves 1, 3, and 5) and underwater (curves 2, 4, and 6) for an adhesive films of thickness \(h = 750 \mu m\). Curves 1 and 2 correspond to smooth, unstructured films, curves 3 and 4 are for the structured films with air-filled channels, and curve 5 and 6 are for the films with channels filled with the silicone oil. It is evident that the presence of subsurface embedded microchannels enhances adhesion both in air and underwater. In our earlier work, we have shown that an embedded air-filled microchannel sufficiently close to the surface can arrest crack propagation.\textsuperscript{15} A higher critical tensile stress is required to initiate a crack, whereas its propagation occurs at a significantly lower stress levels. However, when a propagating crack encounters a channel, a part of the elastic strain energy is dissipated and the crack opening has to be reinitiated, requiring an extra energy penalty. A similar effect has also been reported previously for surface incisions that promote crack arrest at the surface discontinuities.\textsuperscript{21–26} As the processes of crack arrest and crack initiation are independent of change in surface chemistry, we expect the same mechanism to also remain applicable underwater. We indeed observed the same crack arrest effect by the channel when the adhesive was submerged underwater. While curve 3 shows the crack arrest effect of air-filled microchannels in air, curve 4 shows the same when the adhesive was kept underwater.

When the microchannels were filled with silicone oil having surface tension same as that of PDMS \(\gamma_{op} \sim 22 \text{ mJ/m}^2\), it exerts a negative capillary pressure on the wall of the channel \(\Delta P = 4(\gamma_{op} - \gamma_{PDMS})/d\), where the interfacial energy between silicone oil and PDMS surface \(\gamma_{PDMS} \sim 0\). However, pressure far away from the capillary remains atmospheric, resulting in a lateral compressive stress, \(\sigma_{\text{comp}}\), applied on the thin elastica of thickness approximately \(h - d\) over the capillary.\textsuperscript{15} When the adhesive layer is allowed to relax, the elastic stresses manifest as buckling of the thin elastic layer on top of the capillaries. If adhesive contact is made before the surface relaxes or if the surface bumps are removed to make a full adhesive contact by pressing, the capillary pressure-induced compressive stress is regenerated. Equating the corresponding forces yields the relation \(\sigma_{\text{comp}} = 2\pi \gamma_{op}/(h - d)\) which shows that the compressive stress increases with the channel diameter. The typical values of this compressive stress

\(\gamma_{PDMS} = 27.65\)–27.71 mJ/m\(^2\).

can be obtained by using representative values, e.g., for $h = 750 \mu m$ and $d = 710 \mu m$, $\sigma_{comp}$ is estimated as $3.5 \times 10^3 N/m^2$. This compressive stress is small with respect to the critical tensile stress that is to be maintained at the opening of the crack for its continuous propagation on a smooth adhesive surface, $\sim 3.3 \times 10^4 N/m^2$.27,28 Nevertheless, it decreases the stress level at the crack tip. In order to compensate for this negative effect, the contactor is now lifted more to initiate an arrested crack at the vicinity of a channel. It is easy to show that inside an aqueous environment, too, the oil within the channel can exert the same negative pressure. Because here the capillary pressure exerted on wall of channel is estimated as $\Delta P = 4(\gamma_{PW} - \gamma_{PO})/d$, where $\gamma_{PW}$ is the interfacial energy of PDMS/water. Since the water contact angle on PDMS is $\theta_{PW} \sim 95^\circ$, Young’s equation $\gamma_{PW} = \gamma_{P} - \gamma_{W} \cos \theta_{PW}$ yields $\gamma_{PW} \sim \gamma_{P}$, which implies that the presence of water does not diminish the capillary effect significantly.24 This is indeed evident from curves 5 and 6 of Figure 1b which shows that the lifting force for oil-filled channels remains similar when kept in air and underwater.

From Figure 1b, it is also evident that adhesion underwater is somewhat stronger than in air, not only for the case of oil-filled channels (curve 6) but also for the unstructured films (curve 2) and for the air-filled channels (curve 4). This observation can be interpreted in terms of hydrophobic attraction in water. Considering both the silanized contactor and PDMS surface to be nonpolar, work of adhesion underwater can be estimated as $W_{A\text{water}} = -\gamma_W \cos \theta_{PW} - \gamma_W \cos \theta_{SW} + W_A^\text{air}$, where $W_A^\text{air}$, $W_A$, and $\cos \theta_{SW}$ are work of adhesion in air, work of adhesion underwater, and water contact angle (WCA) on silanized contactor, respectively.29 WCA on a PDMS film is about $95^\circ$, and that on a silanized contactor is about $105^\circ$. Using these values in the relation between $W_A^\text{air}$ and $W_{A\text{water}}$, it is concluded that the work of adhesion in water for a silanized contactor and a PDMS film should be around $24 mJ/m^2$ higher than the work of adhesion in air. This estimate is in agreement with the experimental result shown in Figure 2a, which shows that the work of adhesion for a smooth film in air ($\sim 60 mJ/m^2$) increases somewhat underwater ($\sim 70 mJ/m^2$). In essence, it is energetically unfavorable for water to wet the newly created hydrophobic surfaces on separation. This situation essentially creates a vacuum zone at the crack tip, which in turn makes it difficult to peel and increases the peeling force. These observations corroborate well with those of other researchers who reported a higher adhesion energy required to detach two hydrophobic surfaces underwater.30,31 In addition to this, for films with air-filled channels in aqueous environment, trapped air inside the channel could also exert a negative capillary pressure when the air-side contact angle in water is substantially smaller than $90^\circ$. This effect would be similar to the effect of filling the channels with silicone oil in air. However, the WCA on PDMS surface being just slightly higher than $90^\circ$, this effect is minimal for the case studied.

Further, we investigated the effect of surface energy of the contactor on adhesion. In this experiment, a clean contactor with surface energy $\sim 150 mJ/m^2$ was used instead of a low-energy, hydrophobic silanized contactor. The result is shown in Figure 2a. It is observed that adhesion in air for a high-energy contactor is more compared to that for a silanized glass contactor, for both a smooth film and a film with subsurface channels. This is expected, but a straightforward estimate of the increase in energy is close to $130 mJ/m^2$, whereas the actual increase observed is $\sim 250 mJ/m^2$. This observation may be understood by noting that adhesion failure requires greater stretching of the film when surface adhesion is stronger. As the commercial PDMS has some inherent bulk viscoelasticity, more stretching of the film would lead to more viscous energy dissipation. However, for the high-energy hydrophilic glass contactor (WCA $\sim 0^\circ$), adhesion underwater was weaker than in air. The hydrophilicity of the contactor now plays an adverse role in adhesion underwater because water could easily wet the surface of the contactor and the interfacial energy of adhesion thus declines. This is in contrast with the observation for a hydrophobic contactor which shows higher adhesion in water. This observation is depicted in the bar chart of Figure 2a. Here the first set of the bars is for adhesion between PDMS and silanized contactor, and the second set is for adhesion between PDMS and acid-cleaned contactor. Clearly, adhesive

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(27) For an unpatterned film the critical stress $\sigma_c$ at the opening of the crack is estimated by following the analysis presented in ref 23. The experimental data of lift-off height vs crack length are reported in the Supporting Information, Figure S1.


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energy for hydrophilic contactor is more than that for a hydrophobic contactor as adhesion is more between a high-energy and a low-energy surface than between two low-energy surfaces. However, for hydrophobic contactor, adhesion is more underwater (hatched) compared to in air (smooth), but for hydrophilic contactor, the observation is reverse. This difference between hydrophilic and hydrophobic surfaces is possibly due to the interfacial hysteresis which alters because of surface reconstruction effects in contact with water.\(^{(32)}\) Furthermore, the large error bars for hydrophilic contactor too bear the signature of molecular reorientation of polar groups which can create small-scale surface chemical inhomogeneities.

The effects of surface characteristics were further probed by suitably altering the surface hydrophobicity. For example, the contactors were coated with silane molecules of variety of chain length which resulted in equilibrium WCAs $\theta = 71^\circ \sim 107^\circ$. Adhesion energy in air and underwater for these coated contactors are plotted against water contact angle (WCA) on the contactor shows that adhesion underwater (vis-à-vis that in air) strongly depends on the surface property of the contactor. For hydrophobic contactors (WCA $> 90^\circ$), adhesion underwater is more compared to that in air. As we decrease the WCA, both the adhesion energy increases but rate of increase for adhesion in air is higher than that underwater, resulting lower adhesion underwater for hydrophilic contactors meaning that the water now facilitates the separation. Close to WCA $\sim 90^\circ$ this difference vanishes, and the adhesive energy becomes similar in air and underwater. The solid and broken lines are the guides to the eye. This observation is same for both films with channels and without channels (inset).

found that once adhesion was properly made, the work of adhesion did not decrease with time underwater. On the contrary, the adhesion increased with time! This observation is shown in Figure 3. This observation is equally applicable for smooth films and for the films with air-filled channels and for adhesion both in air and underwater. This increase in adhesion with time can be attributed to different physicochemical changes of the surface, including reorientation of the molecules and groups and filling of any remaining microvoids to ensure a better contact.

**Conclusion**

To summarize, we have demonstrated that a structured elastic layer with embedded microchannels, but with a smooth and nonfouling surface, can work underwater as a glue-free adhesive without any surface chemical modifications. The total energy of adhesion for the microstructured layers used in this study is found to be a factor 10–15 more than a similar unstructured film. An especially attractive feature of the structured adhesive is that the energy of adhesion does not change significantly in going from a dry to a wet environment, so that it should remain robust under variable conditions such as rain and wound drying. For a
hydrophobic contactor, adhesion underwater is slightly more than that in air because of the hydrophobic attraction. For hydrophilic contactor, underwater adhesion is somewhat lower than in air. If the channels are filled with a wetting liquid, adhesion increases both in air and underwater comparably. It has also been shown that adhesion does not decrease with time, which is rather common for glues. This consideration makes the concept of a microfluidic structured adhesive especially suitable for various outdoor, marine, and biological applications.

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**Supporting Information Available:** Plot to get critical stress that is to be maintained at the crack tip for crack propagation. This material is available free of charge via the Internet at http://pubs.acs.org.