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Microfluidic Adhesion Induced by Subsurface Microstructures

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Natural adhesives in the feet of different arthropods and vertebrates show strong adhesion as well as excellent reusability. Whereas the hierarchical structures on the surface are known to have a substantial effect on adhesion, the role of subsurface structures such as the network of microchannels has not been studied. Inspired by these bioadhesives, we generated elastomeric layers with embedded air- or oil-filled microchannels. These adhesives showed remarkable enhancement of adhesion (~30 times), which results from the crack-arresting properties of the microchannels, together with the surface stresses caused by the capillary force. The importance of the thickness of the adhesive layer, channel diameter, interchannel spacing, and vertical position within the adhesive has been examined for developing an optimal design of this microfluidic adhesive.

The feet of different arthropods and vertebrates show a remarkable ability to attach to almost any surface with varying surface properties and roughness (1–6). These biological adhesives not only show high adhesive strength, but they can also be detached rapidly and reused over and over. They are self-cleaning and do not leave any marks or footprints after they walk over a surface. Man-made pressure-sensitive adhesives lack these amazing qualities because their high adhesive strength is derived from their viscoelasticity. Although viscous dissipation increases the work or energy of adhesion, the failure occurs at the bulk of the adhesive rather than at the interface, which prevents a clean separation of the adhesive from the surface and also prevents its reusability. Viscoelastic adhesives are also susceptible to fouling by particulate contamination.

The extraordinary ability of naturally occurring adhesives of animals and insects, in particular, is in part related to the complex and hierarchal structural morphologies of their attachment pads (2–8), which use mechanisms of adhesion other than viscoelasticity (such as, friction, suction, and molecular interactions). Several studies on model textured surfaces (9–14) have shown that surface patterning can enhance adhesive strength remarkably. This is because the crack propagation is arrested when it encounters a surface discontinuity and has to be reinitiated thereafter. Crack initiation requires much higher stress than does propagation of the crack on a smooth surface (10, 11).

Whereas the previous studies have focused on adhesion as an interfacial phenomenon and have thus employed surface-modified and -textured adhesive layers, we show that air and viscous domains or “patterns” buried within the subsurface or bulk phase can have equally important strong dissipative effects on the work of adhesion and, at the same time, offer a clean reversible separation. We embedded microchannels of different diameters at various vertical and spatial positions within cross-linked elastomeric adhesive layers bonded to a rigid substrate (15). A flexible microscope coverslip was then brought into complete contact with this adhesive and lifted vertically from its hanging edge at a constant rate, as shown in Fig. 1A. The flexibility of the adhering coverslip was chosen such that it underwent small bending during peeling. Small bending allows for a precise estimation of the interfacial adhesion strength directly from the force versus displacement measurements. A more general form of the experiment would be to peel an adhesive film bonded to a flexible backing off of another flexible plate. For small bending of the plates, the results for this general geometry are in fact equivalent to the experimental setup employed here by appropriately defining the rigidity of the peeled plate.

The peel experiments (Fig. 1A) on an elastic film (16) with air-filled microchannels shows that the contact line between the film and the plate or the crack does not propagate smoothly, but rather with intermittent arrests and initiations at the location of the channels (Figs. 1A and S2). Thus, the channels act as a barrier for crack propagation on the surface of the film. This aspect is also captured in the plot of the peeling torque \( M = F \cdot a \) against displacement \( \Delta \) of the flexible plate (Fig. 1B), where \( a \) is the distance of the crack from the point of application of the load \( F \). The plot shows the existence of several peaks, the first one corresponding to the formation of the cup-shaped crack at the edge of the film (10, 11) and the subsequent ones appearing because of the arresting effect of the buried channels. With an increase in \( \Delta \), the crack approaches an intermediate channel and remains arrested in its vicinity, whereas \( F \) continues to rise. The torque now increases linearly until it reaches a critical value at which the crack nucleates in the form of a cavity at the other side of the channel, and the torque increases sublinearly thereafter. Finally, the torque decreases sharply after a complete opening of the crack and its catastrophic propagation. The average maximum torque, \( \mathcal{M}_{\text{max}} \), at which the cracks initiate is plotted in Fig. 1C, which shows that with an increase in the film thickness, \( \mathcal{M}_{\text{max}} \) varies nonmonotonically, exhibiting very little influence of the channel for both a thick and a thin film. In essence, when the film thickness approaches the channel diameter, the influence is similar to that of adhesion on a fibrous or patterned surface, whereas for very thick films, adhesion is similar to a smooth surface.

For the films thinner than the one with the maximum torque (~100 μm in Fig. 1C), the channels effectively partition the film into smaller portions, which enhances their compliance and consequent crack blunting, as is also seen in the context of adhesives with surface fibrils (17–19). To counter this effect of crack blunting, excess energy is required to initiate the crack, which eventually gets dissipated after its propagation. The effect of crack blunting is weaker for thin films but becomes more important with an increase in the film thickness, requiring larger crack-initiation torque. Hence, the maximum crack-initiation torque \( \mathcal{M}_{\text{max}} \) increases initially with film thickness \( h \), as shown in Fig. 1C. Beyond a threshold thickness (~100 μm in Fig. 1C), the volume fraction of the channels in the

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film is too small to cause any effective partitioning of the film. Consequently, less torque is now required to initiate the crack from the vicinity of the channel. Finally, the effect of the channel becomes almost nonexistent for a very thick film. This situation prevails irrespective of the vertical position of the channel in the film (fig. S3).

The horizontal spacing \( s \) between the channels affects the \( M_{\text{max}} \). Figure 1D shows that for interchannel spacing \( s = 3 \) mm, the \( M \) versus \( \Delta \) plot is characterized by the intermittent peaks corresponding to the arresting effect of the channels, but for \( s = 0.5 \) mm the channels are close enough that the effect of each individual channel is no longer felt. However, one sees a constant torque that is still substantially higher than is required to drive the crack over a smooth film. This result is in accordance with observations on surface-patterned adhesives where a constant torque is also observed \((10,11)\) when the spatial dimensions of the patterns are decreased below a characteristic stress-decay length, \( k^{-1} = \left( \frac{\mu L}{D} \right)^{1/2} \) \((20)\). The later is a material length scale that signifies the distance from the contact line within which the stresses in the film remain concentrated. For the experiment corresponding to Fig. 1D, \( D = 0.02 \) Nm, \( \mu = 1.0 \) Mpa, and \( h = 120 \) \( \mu \)m (where \( D \) is the flexural rigidity of the adhering plate, and \( \mu \) is the shear modulus of the film), and this threshold distance \( k^{-1} \approx 3.14 \text{ mm} \). Therefore, the effect of individual channels is not felt when \( s \sim k^{-1} \).

We now show that the adhesion is considerably enhanced when the channels are filled with liquids of appropriate surface tension and viscosity. Channels of diameter \( d = 50 \) to 1090 \( \mu \)m, embedded in elastic films of \( h = 90 \) to 1500 \( \mu \)m, were filled with silicone oils of viscosity \( \eta = 5 \) to 50,000 cP and surface tension \( \sigma = 22 \) mJ/m\(^2\). Although these oils wet the surface of polydimethylsiloxane (PDMS), they do not diffuse into the network of PDMS in the time scale of the experiments (~10 min). However, being a wetting liquid, the oil results in a negative capillary pressure of magnitude \( \Delta \sigma = 4(\gamma_s - \gamma_d) / d \) inside the channel and also in the vicinity of its elastic wall; away from the wall, the pressure in the film remains atmospheric. Here, \( \gamma_s \approx 22 \) mJ/m\(^2\) and \( \gamma_d \approx 0 \text{ mJ/m}\(^2\) are the surface energy of the PDMS elastomer and the interfacial energy of the elastomer and silicone oil, respectively. This stress field around the channel, resulting from the lateral and vertical asymmetries, effectively leads to a situation similar to that of an elastica under a compressive axial load. This leads to buckling and bulging out of the elastic wall of the channel. Figure 2B depicts the deformation profiles \( \delta \) at the surface of the films obtained by optically scanning their surface in a direction perpendicular to the orientation of the channels. For thinner films (for example, those with \( h = 90 \) \( \mu \)m and \( d = 50 \) \( \mu \)m), the deformation bulges appear as spikes with narrow peaks that do not allow the plate to come in complete contact with the film. However, as \( h \) increases, the deformation flattens out, resulting in a complete contact with the contactor. For small deformations (i.e., \( \delta / d \ll 1 \)), the elastic energy of the surface bulge scales as \( (\mu / d) \delta^2 \gamma_s h / d \), where \( \gamma_s \) is the length of the channel. This increased elastic energy is supplied by a fraction of the reduction in the interfacial energy \( \gamma_s \approx \gamma_s h / (d - h / 2) \), and all of the data fall on a single straight line (Fig. 2C), with the result \( \delta = 1.5 \times 10^{-3} \text{ d} / \sqrt{h} \). When a flexible plate is peeled off of these thicker films, as in Fig. 1A, we obtain the \( M \) versus \( \Delta \) plots (Fig. 3A) consisting of intermittent peaks that correspond to crack initiations and arrests, similar to the observation shown in Fig. 1B with the use of air-filled channels. However, here the bulging induced compressive stress at the interface plays an important role in enhancing \( M \). Whereas peeling causes tensile stress at the crack front \((10)\), the compressive stress in the capillary diminishes it. Consequently, as compared with a film without channels, the plate now has to be lifted more in order to attain the necessary critical stress to drive the crack. Although it is natural to think that viscous dissipation inside the channel should also contribute to the additional torque needed to initiate the crack, experiments with oils show that \( M_{\text{max}} \) does not alter significantly (table S1) when the peeling rate is varied over two orders of magnitude \((3 \text{ to 100 m/s)\). Furthermore, when the liquid viscosity is varied systematically, both \( M_{\text{max}} \) and the adhesion energy increase until an optimum viscosity \((100 \text{ to } 1000 \text{ cP}) \) is reached, beyond which they decrease.

The adhesion strength \( G \) is obtained by integrating the area under the \( F \) versus \( \Delta \) curve (Fig. 3B). A decline in \( G \) for high-viscosity oils may occur because the relaxation time of the high–molecular weight oils can be substantially longer than the time scale in which the crack crosses the channel leading to lower viscous dissipation. Also, high–molecular weight oils would show elastic, rather than viscous, response at short time scales of crack propagation. These observations suggest that the enhancement of torque is mediated not so much by the viscosity of the liquid as by the pressure inside the capillary and the deformability of the film. Both of these aspects were investigated by systematically varying the \( h \) and \( d \), while filling them with a viscous liquid. Figure 3C summarizes a typical

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**Fig. 1.** (A) Schematic of the experimental setup where a flexible plate is lifted from its end off of an elastic adhesive layer with embedded microchannels. (B) \( M = F - \sigma \) is plotted against \( \Delta \) of the flexible plateCurves 1 to 3 correspond to \( h = 80, 150, \) and 200 \( \mu \)m, respectively; \( \mu = 1.0 \) Mpa; and \( D = 0.02 \) Nm. Here, the first peak represents initiation at the sharp edge of the film, and the subsequent peaks capture the effect of each microchannel on peeling. (C) Variation of the \( M_{\text{max}} \) with \( h \). The green horizontal line indicates the torque applied on a plate for peeling off of a smooth film, and the dashed line is a guide to the eye. Triangles represent the maximum torque at which the crack initiates, and error bars represent SD. (D) The effect of \( s \) between the channels on maximum \( M \). Curves 1 and 2 correspond to peeling a flexible plate of \( D = 0.02 \) Nm off of films having multiple channels placed at \( s = 0.5 \) and 3 mm apart.
series in which \( d \) is kept constant while \( h \) is varied. \( G \) increases as the skin thickness \( t = h - d \) is decreased, except for very small values of \( t \) for which \( G \) decreases. This implies that maximum enhancement of \( G \) is achieved at an intermediate thickness of the film dictated by the liquid pressure inside the channel. A similar set of experiments with channels of different diameters shows that \( G \) is optimally enhanced at intermediate ranges of channel diameter (700 to 800 \( \mu \)m) and liquid viscosity (100 to 1000 cP). Figure 3D illustrates a comparison of the optimal microfluidic adhesives with an unstructured adhesive and with a surface-textured adhesive. \( G \) increases by one order of magnitude to ~750 mJ/m\(^2\) when the film is embedded with air-filled channels of \( d = 710 \mu \)m. This is similar to the performance of a surface-textured adhesive because in this case, \( d \) is nearly the same as \( h \). \( G \) increases further to 1600 mJ/m\(^2\) when these channels are filled with an oil of intermediate viscosity. This remarkable enhancement in \( G \) by about a factor of 25, compared to otherwise similar but smooth adhesives, is achieved without incorporating any viscoelasticity in the adhesive but by simply manipulating the pressure inside the subsurface channels.

We now show that the same elastic layer can be used both as a strong adhesive and an easy-release coating. In this context, the nonmonotonic dependence of \( G \) on \( t \), as in Fig. 3C, motivated us to embed two layers of channel within the adhesive at two different vertical locations. When the channels of diameter \( d = 50 \mu \)m of the top layer \((t_1 = 120 \mu \)m and \( t_2 = 300 \mu \)m\)) are filled with oil while those at the bottom layer contain air at atmospheric pressure, the deformations at the surface of the film (similar to \( h = 90 \mu \)m in Fig. 2B) do not allow the plate to come in contact with the film. The layer then behaves like a release coating. However, when the channels at the bottom layer are filled with oil of \( \eta = 380 \) cP while those at the top contain air, the peel experiment yields the \( M \) versus \( \Delta \) plot with characteristic peaks at the location of the channels, as shown in Fig. 3E. This result shows that the same film can be used as a strong adhesive and a release coating without altering the intrinsic rheological or surface properties of the film.

In contrast to the known mechanisms of enhancing adhesion by surface patterning, hairy structures, and chemical modifications with sticky molecules, we have presented a mechanism for greatly enhancing and modulating adhesion by embedded subsurface liquid-filled microchannels in an adhesive layer. A spatial segregation of the elastic and viscous domains allows for a clean and reusable separation of the elastic surface, unlike the conventional viscoelastic adhesives. The confined liquid in the microchannels not only leads to viscous dissipation when a crack passes over it but, more importantly, exerts compressive stress on the flexible wall, which causes the formation of bumps on the film surface. These can either diminish or enhance the stress concentration and adhesive energy during separation. Our mecha-

Fig. 2. Surface deformation of the film due to liquid pressure inside channel. (A) Top view of a typical adhesive film \((h = 120 \mu \)m, \( d = 50 \mu \)m\)) with embedded channels partially filled with silicone oil of \( \eta = 380 \) cP. (B) Liquid pressure inside the channels deforms the film and creates microscopic ridges of height \( \delta \) at the surface. The figure shows the dimensionless height \( \delta/h \) along the direction of propagation of the contact line. (C) \( \delta \) is plotted against the scaled diameter of the channels \( d \), where \( \zeta = d/(h - d/2) \). Error bars represent SD in \( \delta \).

Fig. 3. Peeling off an elastic film with embedded microchannels filled with silicone oil of varying viscosity. (A) \( M \) versus \( \Delta \). Curve 1 corresponds to \( h = 300 \mu \)m and \( d = 50 \mu \)m for channels filled with air. Curves 2 and 3 correspond to \( \eta = 380 \) cP, \( h = 570 \) and \( 750 \mu \)m, and \( d = 530 \) and \( 710 \mu \)m, respectively. (B) Bar chart depicting \( G \) when the channels of diameter \( d = 50 \mu \)m embedded in film of thickness \( h = 300 \mu \)m are filled with air and liquids of different viscosities. (C) \( G \) is varied systematically while keeping \( d = 530 \mu \)m unaltered. The channels are filled with a liquid of \( \eta = 380 \) cP. Error bars represent SD. (D) While on a smooth film (1), the adhesion strength is estimated as \( G = 60 \) mJ/m\(^2\) (similar to that obtained by Johnson et al. (21)); on an incision-patterned film (2) and on a film of thickness \( h = 750 \mu \)m embedded with air-filled channels of diameter \( d = 710 \mu \)m (3), \( G \) is 750 mJ/m\(^2\). \( G \) increases to ~1800 mJ/m\(^2\) when these channels are filled with liquid (4). (E) Schematic of an adhesive film embedded with channels arranged in two different layers with skin thicknesses \( t_1 \) and \( t_2 \) respectively. When the peel experiment is done on this adhesive with the channels of the bottom layer filled with oil while those at the top contain air at atmospheric pressure, the \( M \) versus \( \Delta \) plots are characteristic of crack arrests and initiations at the location of the channels.
FKF1 and GIGANTEA Complex Formation Is Required for Day-Length Measurement in Arabidopsis

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Precise timing of CONSTANS (CO) gene expression is necessary for day-length discrimination for photoperiodic flowering. The FLAVIN-BINDING, KELCH REPEAT, F-BOX 1 (FKF1), and GIGANTEA (GI) proteins regulate CO expression in Arabidopsis. We demonstrate that FKF1 and GI proteins form a complex in a blue-light-dependent manner. The timing of this interaction regulates the timing of daytime CO expression. FKF1 function is dependent on GI, which interacts with a CO repressor, CYCLING DOF FACTOR 1 (CDF1), and controls CDF1 stability. GI, FKF1, and CDF1 proteins associate with CO chromatin. Thus, the FKF1-GI complex forms on the CO promoter in late afternoon to regulate CO expression, providing a mechanistic view of how the coincidence of light with circadian timing regulates photoperiodic flowering.

Many plants monitor seasonal changes in day length to regulate flowering time for successful reproduction (1). In Arabidopsis, regulation of daytime CO expression is the primary process of time measurement in the photoperiodic flowering pathway (2, 3). FKF1 and GI proteins positively regulate CO transcription (4, 5). FKF1 and GI gene expression has similar diurnal patterns (5, 6), which implies that these proteins may interact to regulate CO. We tested their direct interaction in yeast and found that FKF1 interacts with GI (Fig. 1A). Our results, obtained using truncated FKF1 proteins, suggest that this interaction occurs through the FKF1 LOV (Light, Oxygen, or Voltage) domain (Fig. 1A). In addition, the GI N terminus was sufficient to interact with FKF1 (fig. S1).

To assess whether this interaction occurs in vivo, and whether it is modulated by photoperiod or light conditions, we generated transgenic plants constitutively expressing both haemagglutinin (HA)–tagged FKF1 (HA-FKF1) and tandem affinity purification (TAP)–tagged GI (GI-TAP) proteins [35S::HA-FKF1 35S::GI-TAP lines (7)] for coimmunoprecipitation experiments. In the 35S::HA-FKF1 35S::GI-TAP line, a similar amount of GI-TAP protein was precipitated at every time point in both long-day (16 hours light and 8 hours dark) and short-day (8 hours light and 16 hours dark) conditions (Fig. 1, B and C). HA-FKF1 protein was coimmunoprecipitated with GI-TAP protein (Fig. 1, B and C), demonstrating that GI-TAP and HA-FKF1 proteins form a complex in vivo. In both day-length conditions, the amount of coimmunoprecipitated HA-FKF1 protein increased until 4 hours after light onset, remained constant for the rest of the day, and declined in the dark (Fig. 1, B and C), which suggests that light or the circadian clock modulate the FKF1 and GI interaction.

We therefore analyzed the interaction in dark-grown samples. A minimal amount of HA-FKF1 was coimmunoprecipitated with GI-TAP protein in the dark (Fig. 1D), indicating that this interaction is light dependent. In addition, as little as 10 min of light exposure resulted in a marked increase in the amount of FKF1 and GI interaction (fig. S2).

Next we analyzed how light quality (wave-length) affects this interaction. Similar amounts of FKF1 and GI interacted in blue-light–irradiated samples (Fig. 1E) compared with white-light grown samples, but little interaction was observed in red-light irradiated samples (Fig. 1F), indicating that blue light induces this interaction. Further analysis revealed that the FKF1 and GI interaction is fluence rate–dependent (Fig. 1G).

Because we have shown that the FKF1 LOV domain can absorb blue light (5), we postulated that the LOV domain may function as a blue-light-sensing domain for this interaction. We first tested whether FKF1 and GI proteins by themselves are sufficient to reconstitute the light-dependent interaction in vitro (7). FKF1-LOV protein was copurified with the glutathione S-transferase–fused GI N terminus (GST-GI-N) protein incubated under light (Fig. 1G). We then analyzed the importance of the FKF1 LOV domain for light-induced interaction with GI by using FKF1 LOV variants containing three different photochemically blind mutations [C91A, R92D, and Q163L (8–11)]. All three blind mutations attenuated the light-dependent interaction (fig. S3). These results suggest that FKF1 controls the interaction with GI by absorbing blue light through the LOV domain.

To determine more accurately when this interaction occurs in vivo, we performed immunoprecipitation analysis using a transgenic line [FKF1::HA-FKF1 GI::GI-TAP / fkJ1 gis-2 (7)] in which both tagged FKF1 and GI expression are regulated by endogenous promoters (fig. S4). Under long-day and short-day conditions, GI-TAP protein was expressed throughout the day with an afternoon peak, whereas HA-FKF1 expression largely occurred in the late afternoon (Fig. 2, A and B) (5, 12). In long days, the peak expression of FKF1 and GI proteins coincided (Fig. 2A). The HA-FKF1 and GI-TAP interaction was observed in the late afternoon (Fig. 2A), when daytime CO expression occurs (Fig. 2E) (4, 13). In short days, HA-FKF1 peaked about 3 hours later than the GI-TAP peak expression.