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Al Crosby, *University of Massachusetts - Amherst*

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Designing Model Systems for Enhanced Adhesion

Edwin P. Chan, Christian Greiner, Eduard Arzt, and Alfred J. Crosby

Abstract

Nature provides inspiration for enhanced control of adhesion through numerous examples ranging from geckos to jumping spiders. The primary strategy in these examples is the incorporation of patterns, specifically high-aspect-ratio topographic features, to ingeniously maximize adhesion forces while maintaining ease of release. Recently, considerable research efforts have been devoted toward the understanding, development, and optimization of synthetic analogues to these examples in nature. In this article, we provide insight into the mechanisms that lead to enhanced control of interfacial properties through patterning, the strategies that can be used for fabricating synthetic patterns, and an overview of experimental results that have been used to gain understanding and guidance in this emerging field.

Introduction

Recently, biologists have studied the amazing ability of insects and geckos to firmly attach and rapidly detach on demand to a variety of natural terrain.^{1–10} Their ability to control adhesion (attachment and detachment from a surface) is in many cases connected to the long, fibrillar hyperstructures that decorate their attachment pads (see Figure 1a for micrographs comparing the attachment pads of the beetle, fly, spider, and gecko). Depending on the animal species, the fibrils can vary in complexity (sometimes hierarchically arranged), dimensions (fibrils spanning from nanometers to millimeters in diameter), and materials properties. The gecko foot in particular possesses keratinous hairs (setae), 30–130 μm long and containing hundreds of projections terminating in 200–500-nm-wide spatula-shaped structures (Figure 1a, D). These structures maximize adaptability and adhesion to a variety of rough surfaces,^{11–13} facilitate easy release from the surface, and enable attachment and detachment over millions of cycles.^{14,15} Recent experimental investigations have demonstrated that the origin of the adhesion force is a combination of van der Waals interaction and capillary effect.^{16,17}

For materials engineers, there is tremendous opportunity for adopting these natural inspirations in the design of patterned adhesives for a variety of applications. These “smart” adhesives can potentially demonstrate high adhesive force, ease of detachment from any surface, and self-cleaning properties to enhance repeated use. However, much like biological evolution that selects the efficient fibrillar structure for a specific species, we must explore the significant parameter space (Figure 1b) that potentially contributes to these advantageous surface properties. In this article, we provide background based on our current understanding of adhesion, especially in the context of patterned surfaces, and present an overview of experimental results that have led to insight and guidance for future optimization of these interesting properties.

Theoretical Design of Adhesives Definition of Adhesion

Adhesion describes the energetic processes during the formation and separation of an interface between two materials. It is not a property of one material but

rather a unique property of the combination of materials. The thermodynamic definition of adhesion involves the work, or energy, associated with the creation of an interface from two surfaces:

$$w = \gamma_1 + \gamma_2 - \gamma_{12}, \quad (1)$$

where γ_1 and γ_2 are the free surface energies of the original materials and γ_{12} describes the energy of the interface after formation.¹⁸ Therefore, large free surface energies relative to the interfacial energy imply a greater resistance to separation, that is, greater adhesion. Conceptually, this definition is straightforward, but its practical use and relationship to real materials are quite limited.

In practice, the energy of interface formation differs greatly from the energy associated with separation. In fact, for polymer interfaces, the energy of interfacial separation can be orders of magnitude greater than the energy of interface formation. A common example of this discrepancy is the adhesion of pressure-sensitive adhesives, such as tape, to glass. For these materials, the energy for interface formation is approximately 0.1 J/m², whereas the work of separation can be as large as 1000 J/m².¹⁸ This discrepancy implies that history-dependent processes play a dominant role. These history-dependent processes can include molecular interactions strictly at the interface or in the near-interface bulk regions. Therefore, the adhesion of an interface is a multiplicative property related to the interfacial and bulk properties of both materials.

The decoupling of the interfacial and bulk contributions has been a consistent theme of research in the field of adhesion for the past several decades.^{19–29} It reflects similar efforts in fracture mechanics, where the stability of a crack in one material depends on a balance of interface and bulk effects.

Influence of Pattern: The Principle of Contact Splitting

At first glance, it seems counterintuitive that removing material from a contact region can enhance adhesion. Theoretical and experimental evidence has accumulated to show that patterning, that is, splitting one solid contact into many finer ones, is beneficial. This principle, termed “contact splitting,”³⁰ can be understood from the following examples.

First, in peeling one material from another material at an interface (Figure 1c), the applied force (P_y) scales with the width (w_y) of the interface by the interfacial adhesion (G_y).³¹

Figure 1. Examples of natural and synthetic fibrillar attachment structures. (a) The attachment foot pads of the beetle, fly, spider, and gecko. They consist of a hierarchical arrangement of fibrillar structures called setae. The tips of the fibrils are terminated by flat plate-like structures called spatulae (circled). (Figure reproduced from Reference 30.) (b) Schematic illustration of a representative synthetic fibrillar analogue, highlighting the vast parameter space that can be controlled to optimize the adhesive properties of the materials system. (c), (d) Examples demonstrating the principle of contact splitting. For both examples, the separation force of the patterned adhesive (P_n) increases with the total number of split-up contacts (n), which illustrates that the enhancement in strength is associated with the increase in contact line, as opposed to contact area. (c) In a peel geometry, $P_n \sim n^{1/2}$. (d) In a flat punch geometry, $P_n \sim n^{1/4}$. G_c is interfacial adhesion, a_s is the smooth contact radius, E^* is the reduced Young's modulus, and P_s is the separation force for a smooth reference.

$$P_s = G_c w_s \quad (2)$$

Therefore, peeling a wider piece of tape requires more force than peeling a thinner piece of tape. If all regions of a representative patterned area peel simultaneously, then for a close-packed arrangement of n regions (Figure 1c), the increase in interfacial width scales as $n^{1/2}$. Thus, the total peel force P_n also increases as $n^{1/2}$ for a

patterned interface as compared with a nonpatterned interface. The dependence on the contact line (perimeter), not contact area, for controlling adhesion was demonstrated by several research groups in the study of patterned adhesion control.^{32,33} Although this simple relationship demonstrates that the maximum separation force can be increased, the total energy of separation will actually decrease, because of a

decrease in interfacial contact. The only way for patterns to increase both total force and total energy is for the energy associated with initiation of separation at the perimeter of an individual post to be greater than the energy of propagation away from the perimeter. This situation can be caused by differences in mechanical constraint at a physical edge and has been demonstrated to cause significant

increases in adhesion in synthetic patterned interfaces.^{32–35}

A second example of how patterns can alter the interfacial contribution can be understood by considering the perpendicular separation of a post from a flat surface (e.g., a finger pulling away from a sticky surface) (Figure 1d). It is straightforward to demonstrate that the force to separate n posts (P_n) scales directly with the separation force of a single post (P_s):³⁶

$$P_n = n^{1/4} P_s. \quad (3)$$

This scaling changes if the posts are terminated with spherical caps of curvature R . In this situation, the theory of Johnson, Kendall, and Roberts (JKR theory)³⁷ combined with a self-similar definition of the local curvature³⁰ predicts that

$$P_n = n^{1/2} P_s. \quad (4)$$

Regardless of the exact scaling, these examples indicate that the interfacial

strength is enhanced by decreasing the diameter of the fibrils.³⁸ Similar to the peeling examples, the energy of separation is enhanced only if the initiation energy is greater than the propagation energy.

These example mechanisms only consider energy dissipation at the interface, but the three-dimensional (3D) geometry of a patterned interface also plays an important role. The aspect ratio of the features increases conformability to the contacting surface. Higher-aspect-ratio features are more compliant, which improves their adaptability to rough surfaces and maintains interfacial contact. This mechanism cannot be overemphasized, as adhesion is most dependent upon the ability of two surfaces to establish contact. Additionally, the aspect ratio (λ) of the fibrillar structures defines the constraint at the interface. Less constraint leads to a decrease in the stress concentration along the interface. In other words, increasing the aspect ratio of the features effectively “blunts” an interfacial crack during separation.

Besides G_c , n , and λ , there are many other parameters that influence the development and measurement of adhesion for a patterned interface. A summary of some critical parameters is shown in Figure 1b. In addition to physical parameters, processing limitations also play a role in practical design. One limitation for high-aspect features is the tendency for nearest-neighbors to collapse because of interfeature attractive forces. Also, the ultimate fracture force of the fibrils decreases as the fiber diameter decreases, thereby limiting the smallest practical feature size. Spolenak et al. theorized the balance of these design parameters in adhesion maps for patterned surfaces (Figure 2),³⁹ but a complete experimental verification has yet to be established.

Quantifying Adhesion

For elastic materials at a nonpatterned interface, adhesion is often described by the critical adhesion energy, G_c . This descriptor represents the critical driving

Figure 2. A theoretical adhesion design map illustrating the tradeoff between the materials parameters of fiber radius (R), aspect ratio (λ), contact strength (σ_{app}), and Young's modulus (E) for spherical contact geometry. Several conditions must be met by an efficient fiber system: fiber fracture and condensation must be avoided (regions above the lines “fiber fracture” and “condensation”); adaptability to surface irregularities and sufficient contact area at pulloff must be ensured (left of lines “adaptability” and “ideal contact strength”). This results in the triangular target area for optimizing adhesion. The thin contours are lines of constant apparent adhesion strength. (Figure reproduced from Reference 39.)

force for moving a “crack” at an interface and has units of energy per area. If the applied driving force is greater than a critical value (i.e., G_c), then the interfacial materials will separate. Once G_c is known for a given materials interface, then practical design parameters such as the maximum sustainable force or stress for a given geometry can be determined. Many textbooks and review articles have been written on the measurement of G_c for non-patterned interfaces. Frequently, the contact probe adhesion test is used for both patterned and nonpatterned interfaces.

In contact probe testing, a probe (e.g., a circular punch or spherical cap) is brought into contact with another material, and the established interface is subsequently separated (Figure 3).^{28,32,34,40} During the process of contact and separation, the force (P), displacement (δ), and area of contact ($A = \pi a^2$, where a is the radius) are monitored to provide a complete description of the adhesion properties (Figure 3b and 3c). These measured parameters can be used to calculate G_c in a straightforward manner using existing theories. From G_c , the maximum separation force and stress can be determined. The direct relationship between G_c and these practical adhesion descriptors depends on the probe geometry. For example, for a spherical cap,

$$P_{\text{sep}} = 1.5\pi G_c R, \quad (5)$$

where R is its radius of curvature.^{34,37} For a circular punch of radius a ,

$$P_{\text{sep}} = k(a^3 G_c)^{0.5}, \quad (6)$$

where k is a constant related to the elastic properties of the materials at the interface.³⁶ Based on these relationships, P_{sep} for a spherical cap is independent of elastic properties as well as the maximum contact area, whereas P_{sep} for a circular punch is dictated by both the elastic properties and dimensions of the interface. If we normalize P_{sep} for a circular punch by the interfacial area to define an average stress (σ_{app}), then σ_{app} is still dependent upon dimensions and materials properties:

$$\sigma_{\text{app}} = k_1(G_c/a)^{0.5}. \quad (7)$$

For patterned interfaces, G_c cannot be defined quantitatively; therefore, most researchers have substituted descriptors such as P_{sep} , σ_{app} , and a term called W_{adh} , which is defined as the energy dissipated during the contact and separation of a contacting probe normalized by the maximum contact area.^{32,34} It is important to note that these quantities are useful, but they do not represent absolute properties. For example, W_{adh} will not approach ther-

modynamic quantities for fully reversible materials, and it is dependent upon the maximum contact area. Additionally, P_{sep}

will depend upon the contact history, such as maximum contact force. A summary of the descriptors used to quantify adhesion is presented in Table I.

Additionally, for patterned and nonpatterned surfaces, the measurement of G_c , P_{sep} , and similar descriptors for adhesion are heavily dependent upon the stiffness of the measurement instrument and physical parameters, such as the thickness of the materials.²⁶ These effects have been investigated thoroughly for nonpatterned interfaces and must be considered in comparing measured quantities for patterned interfaces.

Strategies for Fabrication

Top-Down Fabrication Approaches

A majority of the approaches for fabricating structured adhesives are top-down approaches based on lithography, usually a combination of photolithography and micromolding. Photolithography uses light to create patterns on a photoresist, which is a polymer that changes solubility upon light exposure (Figure 4). Hence, patterning the photoresist is accomplished by modulating light with a photomask. Depending on the resist chemistry, the exposed region either becomes soluble or insoluble with a solvent used for subsequent development of the pattern. The final structure is obtained after development (Figure 4a, step 4). The pattern can either serve directly as a structured adhesive or as a master template that is subsequently replicated by molding to obtain the negative structure (Figure 4a, step 5).^{32–34,41–50} Other forms of imprint-based patterning include nanoimprint lithography (NIL) and step-and-flash imprint lithography (S-FIL). For patterning materials on the nanometer length scale, the templates are fabricated using electron beam lithography. NIL patterns polymers by molding a viscous polymer at elevated temperature.⁵¹ In S-FIL, a photopolymerizable monomer is used as the molding material instead of a viscous polymer.⁵²

Whereas photolithography is limited to patterning two-dimensional (2D) structures, the concept can be extended to generate 3D structures. Interference lithography⁵³ and phase-mask lithography⁵⁴ have fabricated 3D microtruss structures in photoresist materials. The resultant structure is replicated by infiltration with a low-viscosity monomer or polymer such as poly(dimethyl siloxane) (PDMS).⁵⁵

As we have highlighted, top-down approaches are quite capable of generating structures with high fidelity. This advantage has led to the first systematic study of

Figure 3. (a) Example of an axisymmetric probe-type contact adhesion test. The test measures adhesion by the formation and subsequent separation of the interface established between the spherical test probe and the adhesive. (b) The results of the adhesion test are summarized by a force–displacement (P – δ) curve. (c) Time history (P vs. t) of the adhesion test, illustrating the formation and separation of the interface. Images show contact area between spherical probe and flat surface. The dark circles define the contact area (πa^2), where a is the contact radius. The scale bar is 500 μm .

Table I: Summary of Adhesion Descriptors Commonly Used to Quantify the Force and Energy of Both Nonpatterned and Patterned Materials.

	Descriptor	Comments	Advantages	Disadvantages
FORCE	P_{sep} separation force	For single fibril: $= 1.5\pi G_c R$ $= (8\pi G_c E^* a^3)^{1/2}$	JKR contact Flat punch contact	Simple quantification of strength
	σ_{app} contact strength	$= \frac{P_{\text{sep}}}{A_{\text{app}}}$	A_{app} is the projected or apparent contact area	Simple quantification of strength
	$\bar{P}_{\text{sep}}$ normalized separation force	$= \frac{P_{\text{sep, pattern}}}{P_{\text{sep, nonpattern}}}$	Straightforward comparison with reference nonpatterned material	Extensive property Ignores contact geometry
ENERGY	U_{adh} total separation energy	$= \oint P \cdot d\delta$	Accounts for total energy needed to form and fail the interface, including dissipative events such as viscoelastic effects	Extensive property Ignores contact geometry
	G_c critical adhesion energy	Defines the critical energy needed to cause the interface to fail spontaneously	Intensive property of the material	Cannot be rigorously implemented to account for viscoelastic effects
		Relevant forms of the expression depend on the contact geometry	Classic descriptor of adhesion	Difficult to measure for patterned interfaces
		For reversible systems, this quantity approaches the thermodynamic work of adhesion		
	W_{adh} work of adhesion	$= \frac{\oint P \cdot d\delta}{A_{\text{max}}}$	A_{max} is the true contact area at maximum compression	Accounts for energy dissipation across a defined contact area
			Practical description of adhesion for patterns	Extensive property Depends on true contact area
	$\bar{W}_{\text{sep}}$ normalized work of adhesion	$= \frac{W_{\text{adh, pattern}}}{W_{\text{adh, nonpattern}}}$	Straightforward comparison with reference nonpatterned material	Extensive property Depends on true contact area

adhesion as a function of pillar diameter and aspect ratio by Greiner et al.⁴⁴ However, there are several inherent limitations that prevent commercial adaptation, including (1) scalability—only a limited area can be patterned at a given time; (2) economics—related to scalability and also due to the expensive optics required; and (3) materials limitations—the structures must be replicated onto the appropriate polymer to generate a structured adhesive.

Bottom-Up Fabrication Approaches

An alternative fabrication approach is bottom-up fabrication, or self-assembly, which relies on energy minimization to assemble basic building blocks into structured materials with well-defined length scales. Anodization, block copolymer self-assembly, and colloidal assembly are

among the established forms of self-assembly.

In anodization, porous aluminum oxide is formed by etching aluminum metal using an electrochemical process.⁵⁶ The resulting membrane pattern is replicated by infiltration with a low-viscosity polymer and enables replication of a variety of polymers to obtain 2D arrays of pillared structures.^{57–59} Similarly, backfilling of a colloidal crystal leads to the formation of an inverted opal structure that mimics the microtruss structures discussed previously.⁶⁰ However, these approaches are merely vehicles for pattern transfer, as they are difficult to implement directly as structured adhesives.

In block copolymers, patterns develop as a result of microphase separation.⁶¹ Because of connectivity between incom-

patible polymer chains, the polymers segregate into discrete domains with length scales corresponding to the dimensions of the polymers—tens of nanometers. These nanostructured materials have served primarily as templates;⁶² however, there is potential for using them directly as patterned adhesives.

Although not classically categorized as self-assembly, many forms of instabilities also generate well-defined structures based on the principle of energy minimization.^{63–77} One example of a scalable instability approach is wrinkling. In wrinkling, the competition between an externally applied compressive stress and materials-defined bending resistance leads to the formation of a wrinkling pattern with well-defined wavelength and amplitude. Because wrinkle formation

Figure 4. A well-established top-down approach for synthesizing patterned adhesives is soft lithography, which consists of photolithography and micromolding.

Figure 5. Bottom-up, or self-assembly, approach for synthesizing patterned adhesives using surface wrinkling to develop well-defined surface patterns. (a) One process for fabricating stable, aligned surface wrinkles for polymers. (b) The process is highly scaleable. (c) The resultant structures can be orientationally and spatially controlled and enable the realization of a variety of wrinkling morphologies. (Adapted from References 67 and 68.)

relies on the development of a compressive stress, many different stimuli can be used, including osmotic,^{63,67,68} thermal,^{74–76} and mechanical stress.^{72,73} A versatile approach for generating surface wrinkles over large areas was recently demonstrated by Chan and Crosby.^{67,68} In their approach (Figure 5), an osmotic stress coupled with lateral confinement drives the formation of surface wrinkles on an elastomer. The lateral confinement is generated by ultraviolet/ozone (UVO) oxidation of a PDMS elastomer, which forms a silicate skin layer, and the osmotic stress is caused by swelling of the PDMS elastomer with a photocrosslinkable acrylate-based formulation. Definition of the primary compressive stress through selective UVO oxidation leads to the forma-

tion of several wrinkling morphologies, including aligned wrinkles,⁶⁸ dimples, and microlenses (Figure 5c).⁶⁷ Besides being highly scaleable (Figure 5b), the wrinkling pattern can be used directly as a patterned adhesive.⁷⁸

Structured Interfaces without Topography

Significant emphasis in patterned adhesion is placed on designing topographic structures. This trend is primarily motivated by the fibrillar structures observed in geckos and many insects. However, alternative forms of structured interfaces including surface-chemical and compositional patterns should not be overlooked. In surface-chemical patterns, the patterns are characterized as a periodic variation in

surface chemistry. These patterns can be fabricated using a combination of photolithography and surface treatments, such as silane chemistry.³⁵ A compositional pattern consists of a periodic variation in elastic and viscoelastic response and adhesion energy.⁷⁹ Block copolymers or even well-defined polymer blends are excellent candidate materials as compositional patterned adhesives. Although these patterns have not been systemically studied, there is significant potential for exploring these systems.

Adhesion Force and Stress-Dependence on Pattern Dimensions

One of the most interesting points when thinking about fibrillar adhesives is the principle of contact splitting. As we dis-

cussed earlier, the division of a contact area into a number of n contact elements enhances separation strength by a factor of n^r , where the exponent r describes the efficiency of the contact splitting for a particular contact shape.⁸⁰ This principle of contact splitting demonstrates the optimization of fibrillar density observed in insects and geckos, that is, larger animals have a higher density of fibrils. The mechanism of contact splitting is similarly observed for synthetic analogues, as demonstrated by comparing the pulloff strength σ_{app} versus fibril radius a_f for a variety of sizes and shapes (Figure 6).

As Figure 6 indicates, smaller fiber radii lead to higher pulloff strength, as predicted by theory. Also, the tip geometry of the fibrils plays an important role in the splitting efficiency of the pattern for adhesion. Among the three tip geometries, it is clear that the mushroom-shaped tips provide the most promising results.^{46,48,81,82} Similar to the fibrils of the gecko, the mushroom design appears to distribute applied energy away from the interface. Most of the applied energy is stored in the smaller, longer "stem," which is significantly more geometrically compliant than the short, wide "cap." Therefore, the energy gained by releasing, or separating, a small area of the cap is insignificant, and the associated driving force for separation is small. Furthermore, the larger dimensions of the cap stabilize neighboring features from nearest-neighbor collapse while maximizing the

packing of the mushroom "caps" and maintaining the benefits of high-aspect-ratio features.

Additionally, the dimensions of individual fibrillar features must relate to the roughness dimensions of the contacting surface to take advantage of the splitting efficiency. This effect was demonstrated with examples from nature,⁸³ as well as synthetic analogues by Crosby et al.³⁴ Low-aspect-ratio pattern features and single-asperity contact adhesion tests revealed that the radius of the feature must be smaller than a critical radius related to the asperity curvature and material-defined length scale. This critical radius also points to the relative importance of initiation and propagation processes, as discussed previously.

Finally, although the results in Figure 6 primarily summarize materials systems with a narrow range of elastic moduli (~1–10 MPa), the modulus of the material will play a significant role in maximizing interfacial contact. Conceptually, an adhesive with a lower modulus will conform more easily to a rough interface as compared with a higher modulus. This concept is well-established in pressure-sensitive adhesives and is commonly referred to as the Dahlquist criterion.⁸⁴ For fibers with high aspect ratios, however, a lower limit in modulus results from the necessity to avoid collapse, or condensation (Figure 2). Thus, the modulus presents an additional materials parameter that must be optimized.

Figure 6. A comparison of published contact strength σ_{app} data represented as pulloff strength versus fiber radius a_f . The dashed curves are empirical fitting lines that demonstrate the contact splitting principle, that is, enhanced strength for progressively smaller fiber radii. Also apparent is the strong effect of geometry in flat, spherical, and mushroom-like contacts.

Summary

Studies on biological systems have clearly demonstrated that the strategy of contact splitting leads to the novel control of adhesion, providing both enhanced strength with manageable release. Inspired by these beautiful examples, several research groups have taken well-established and recently developed methods for patterning materials surfaces to create synthetic analogues of nature.

In this article, we have attempted to highlight some of the mechanisms for pattern control of adhesion through examples and experimental evidence. It is clear that interfacial splitting results in enhanced strength and control, but we are still a long way from completely understanding and optimizing products in this emerging field. How fine can fibrillar structures eventually be made to optimize adhesion? What materials will provide the best properties for repeated use (i.e., self-cleaning)? How will interfaces optimize both strength and release? A large parameter space exists, and special care in the experimental measurements is required to fully develop predictable models and enhanced products that are scalable. In pushing forward, it is necessary to recall the lessons from the well-established field of adhesion while incorporating new breakthroughs in materials science and biology.

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