

# MODULATING ADHESION BY NEAR-SURFACE ARCHITECTURE

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## Abstract

The broad paradigm in understanding and design of adhesives has been that surface chemistry, i.e., inter- and intra-molecular forces, defines “true” or “intrinsic” adhesion. Macroscopic adhesive performance, as measured by one of a variety of experiments such as peeling, cantilever beam, or the like, additionally involves bulk dissipation, typically due to viscoelastic or plastic deformation. This dissipation is linked, usually multiplicatively, to the intrinsic adhesion. Thus, although bulk dissipation often dominates intrinsic adhesion, the latter is critical to activate the former since they are linked serially. The energy required to separate the surfaces at the molecular level, to reach the interface, has to traverse a vast bulk region that extracts its own ‘super’ tax in the form of energy dissipation. While there is a long history of enhancing or controlling this process further by structuring of the material near the interface, this effort has seen tremendous activity in the last decade, spurred primarily by the discovery of biologists that nature has devised microstructures ranging in size from tens of nanometers to many microns and larger to enhance and control adhesion, friction, and surface compliance. In this work we will review briefly the contributions of our group over the last few years to the design and study of bio-inspired, near surface, architectures for controlled surface mechanical properties.

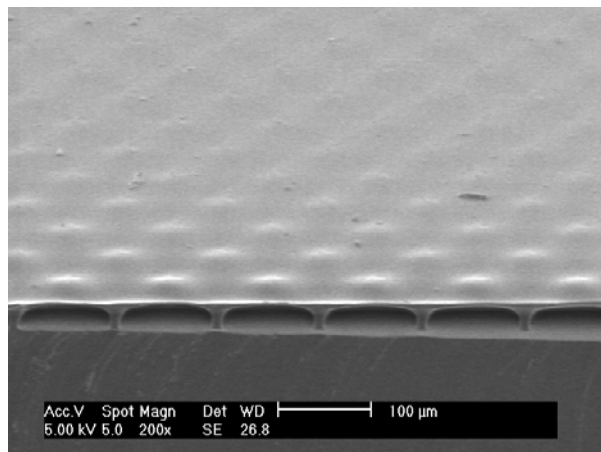
## 1. Introduction

It goes nearly without saying that adhesion depends in the first instance on the bonding and intermolecular interactions at the interface between the adhering materials or bodies. There are two primary metrics for adhesive performance, its strength (with units of stress, Pa or N/m<sup>2</sup>) or the energy supply required per unit area to separate the interface (with units of J/m<sup>2</sup> or N/m)[1]. While one or the other is more useful in any given application, we will here base our discussion on the energy per unit area, which we shall call the work of adhesion. This has generally a better chance of being a true intensive material property. One may speak of an ‘intrinsic’ work of adhesion, that representing the bonding and intermolecular interactions, or of the total work of adhesion, which measures the energy that a remote loading system must supply to the material in order to separate the interface. The difference between the two arises generally due to dissipation because of inelasticity, for example viscoelasticity or plasticity, of the bulk adherends. This dissipation is coupled to the intrinsic work of adhesion, often multiplicatively [2]. There has been considerable work on structuring the near-surface region to modulate – enhance or control – adhesion. The last decade, in particular, has seen quite a concerted effort along these lines, inspired in good measure by biological studies showing that highly controlled and enhanced surface mechanical properties can be achieved by appropriate design of near-interface architecture[3-5]. An interesting general finding to emerge from this body of work is that surface architecture can introduce mechanisms for enhancement and control of interfacial properties at a length scale intermediate between the molecular size of intrinsic adhesion (*nms*)

and that of bulk dissipation (mms or larger). In this report, we review some of the contributions of our group to this work; a broader view of this field is described in a recent review article [6].

## 2. Film-Terminated Architecture

Figure 1 shows a film-terminated fibrillar structure that was designed to capture two essential biomimetic features of natural interfaces in lizards and insects: a fibrillar architecture and a thin terminal film[7]. Though a crack-trapping mechanism, which is activated due to the periodic variation in compliance of the structure, this architecture has strongly enhanced adhesion and static friction (up to a factor of nine) compared to a flat unstructured control[7-9].

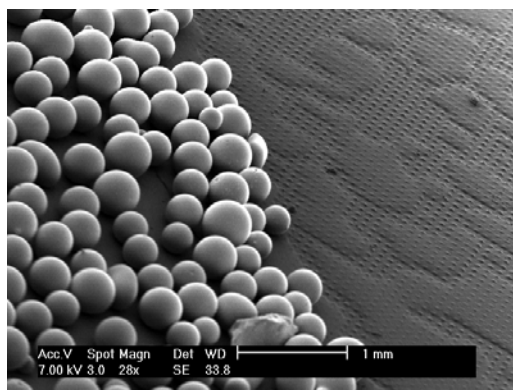


**Figure 1.** Film-terminated fibrillar structure has strongly enhanced adhesion and static friction compared to an unstructured control [10]. (Micrograph courtesy of Nichole Nadermann.)

Moreover, we find that the enhancement of interfacial properties couples multiplicatively to the intrinsic work of adhesion[11]. This last fact has an interesting implication, suggesting that such structuring might provide an independent ‘handle’ to control surface mechanical properties that couples to the near-surface intrinsic adhesion and (perhaps) also to bulk adhesion. In this instance, by choice, the structure was fabricated using a nearly perfectly elastic elastomer, poly(dimethylsiloxane), PDMS, so as to separate the effect of surface structuring from other potential energy dissipating mechanisms such as bulk inelasticity.

## 3. Active Control of Adhesion

The architecture shown in Figure 1 can be designed so that it has two metastable states in which it can exist (Figure 2). One state, the sticky one, corresponds to the micrograph shown in Figure 1. The second, non-sticky state, occurs when the terminal film is pushed into contact with the substrate between the fibrils. With an appropriate design, i.e., choice of film thickness, fibril height, and separation between fibrils, the second state can be stable as well, and one can switch between the two states[10]. Figure 2 shows qualitatively the difference in adhesive properties of two regions on the surface of a sample. One region, in the state shown in Figure 1, is adhesive and particles stick to it. The other, with a collapsed non-stick structure, is not adhesive.



**Figure 2.** Film-terminated fibrillar structure can exist in two metastable states. The flat state is highly adhesive; the collapsed state (on the right part of the micrograph) is non-adhesive. This is demonstrated qualitatively by the fact that particles stick to the adhesive but not to the non-adhesive region. (Micrograph courtesy of Nichole Nadermann.)

Another mode of active control of adhesion was achieved by using a rippled surface. The surface of an elastomer, PDMS, was rippled by oxidizing the surface while stretching it. On release of the stretch, its surface is rippled and its adhesion is strongly attenuated[12]. However, the adhesive property can be recovered simply by stretching the elastomer again. It was shown that this simple structuring of the surface results in mechanically tunable adhesive properties. The rippled surface additionally has the property that its contact adhesion, as measured by a spherical indenter, depends on the pressure applied. In contrast, adhesion of a flat unstructured elastomer does not depend on pressure. This pressure-sensitivity of adhesion arises because at low pressures contact remains partial whereas large pressure can push the indenter into full contact, resulting in greater adhesion on indenter retraction[13].

#### 4. Adhesion Selectivity

Nature very often employs surface architecture for selective adhesion. We have shown that two PDMS surfaces with shallow ripples, if complementary to each other, will adhere very well to each other while rejecting adhesion to other rippled surfaces with different wavelength or amplitude [14]. If one employs a pillar-channel structure, which has much deeper pillars, the adhesion for complementary structures can be enhanced by up to a factor of forty while that of non-complementary structures is strongly attenuated[15]. In both cases, a crack-trapping mechanism works to enhance adhesion in complementary surfaces. For the pillar-channel structures friction additionally contributes to adhesion while misfit dislocations that accommodate relative misorientation limit the ability of complementary surfaces to match each other.

#### 5. Acknowledgements

The support of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award DE-FG02-07ER46463 for this work is gratefully acknowledged. This brief review describes work conducted in collaboration with the groups of Professor C-Y. Hui and S. Yang. The author lists of cited publications reflect individual contributions.

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