Fabrication and Characterization of Bioinspired Functionally Graded Adhesive Materials
H. Shahsavan and B. Zhao, IPR Symposium, University of Waterloo, ON N2L 3G1, Canada

Inspired by the amazing adhesive properties of the insects and lizards, a great deal of investigations has been conducted to manufacture synthetic and biomimetic adhesive commodities. Biological adhesive systems, either flat or structured surfaces, whether wet or dry, utilize long dissipative bonds and maximized real contact area to suppress the contribution of stored elastic energy in breakage of interfaces. Accordingly, viscoelasticity of the soft, smooth and wet toe pads of tree frogs can be deemed as of the basic principles in manufacturing of traditional commercial Pressure-Sensitive Adhesives (PSAs). In addition, material independence, repeatability and flaw tolerance properties of hair-like structures found in lizards’ toe pads introduced them as a unique prototype for new generation of Bioinspired Fibrillar Adhesives (BFAs).

Besides biological adhesives, a plethora of natural substances and animals are benefitted from remarkable bulk resistance to cracking, deformation, and damage, thanking to the gradations of the physical and chemical properties on their exterior surfaces. For example, having the strongest elements located where the stress is the maximum, natural surfaces like bamboos, bones, and plant stems make the best use of gradient in their surface mechanical properties. Functionally Graded Materials (FGMs), the well-known group of materials in materials science, have been introduced and developed based on these principles. Although both FGMs and adhesive materials are well studied in the literature, there has been less attention to combination of them. In fact, graded adhesive structures have been the subject of studies in only a few published works. In our work, we aimed to use principles of FGMs for development of Functionally Graded Adhesive Materials that have more efficient properties comparing to their simple non-graded counterparts. For this, we have fabricated a hybrid adhesive structure consisting of an elastic film-terminated BFA coated with a viscoelastic layer of PSA.

The new hybrid structure demonstrated a remarkable increment of adhesive strength comparing to control samples. In addition, the common extensive bulk deformation of the PSA during the debonding process was drastically hampered. Having both remarkable adhesive strength and structural integrity during the debonding, Functionally Graded Adhesives can be great potentials to be used in industries requiring strong, adaptive, and durable adhesives. In addition, the systematic study on the synergetic effects between the adhesive mechanisms of the PSAs and BFAs provides additional fundamental insights to the current body of the literature. In this talk, we will present some of our latest progress in the development of bioinspired functionally graded adhesive materials as published in.

Experimental
Hexagonal arrays of PDMS micropillars with 50μm diameter, 150μm height and 115μm center-to-center spacing were fabricated through the soft-lithography technique. A 10% weight
mixture of PDMS resin and curing agent (Sylgard® 184, Dow Corning) was poured on a master-mold of micro-holes. The liquid PDMS was cured at 90°C for 1 hr and peeled off gently after curing. Then, the dipping method developed in reference 7 was used to fabricate elastic film-terminated micropillars. The fabricated micropillars in the previous step were placed up-side-down on a thin layer of PDMS which was spun on a glass slide. The thickness of the elastic film was varied from 8 to 24μm. The entire system was placed in the oven at 90°C for 1 hr and peeled off the substrate. At last, a 1.5% weight mixture of PDMS was spun on the fabricated elastic film-terminated fibrillar structure and cured at 90°C for 1 hr. The thickness of the top viscoelastic layer was varied from 18 to 50μm. Resultant samples were hybrid and graded structures consisting of a viscoelastic top-layer and an elastic film-terminated fibrillar interface (B-E12-VE50). Figure 1(a) shows the schematic view of the new hybrid structure and Figure 1(b) shows the SEM micrograph of the film-terminated fibrillar adhesive.

The adhesive properties of the fabricated structures were determined through a series of indentation tests using a custom-made indentation apparatus. Fabricated samples were indented to different preloads by a 6 mm diameter hemispherical fused silica probe with loading and unloading velocity of 1 μm/s. Visual examination of the contact formation and separation processes were performed in real-time with a bottom-view camera. The load-displacement data were measured and recorded with a 0-10 g load cell. Indentation results of the new hybrid structure were compared to that of three control samples. The tested control samples were a flat viscoelastic PDMS layer on glass substrate (VE50), an elastic film-terminated fibrillar interface (B-E12), and an elastic PDMS film coated with a viscoelastic PDMS top layer (P-VE50).

Results and Discussion

Preliminary tests were performed on samples with different thickness of the elastic intermediate and the viscoelastic top layers to determine the optimum adhesive structure. It was revealed that the most efficient adhesive in terms of both adhesion strength and structural integrity is the one with the thinnest intermediate elastic and the thickest top viscoelastic layers 3-5. Accordingly, the remaining of the experiments were carried out on the optimum sample, i.e. B-E12-VE50.
Figure 2 (a) represents typical load vs displacement curves for four tested samples. Except sample B-E12, bonding process of other samples starts with a pronounced snap-in force due to the intermolecular surface forces. The vertical displacement continues up to the point that a certain preload is reached. The unloading process is linear for a remarkable range between the preload and pull-off points. The debonding for the elastic sample B-E12 is rapid and has several small zigzag steps, suggesting the presence of crack trapping mechanism during the separation. The debonding process of the viscoelastic samples is gradual and smooth but undergoes a slope change between the pull-off point and the separation. This slope change is indicative of the bulk deformation processes such as fibrillation, cavitation and other instabilities. The slope change is the most pronounced for the viscous film on PDMS (P-VE50), becomes less for the viscous film on glass (VE50), and is the least pronounced for the new hybrid structure (B-E12-VE50). This observation suggests that the new hybrid structure experiences less bulk deformation while having much greater pull-off force \[3-5\]. In fact, the new type of adhesive is stronger and has better structural integrity comparing to other control samples.

Figure 2 (b) shows the variation of the pull-off force vs preload. Apparently, the preload dependence of the new hybrid adhesive is significantly greater than other control samples. Preload dependence of this structure can be attributed to its graded nature. Functionally graded materials have been shown to have variation of the mechanical properties along the depth of their surface \[6\]. For instance, modulus of elasticity of the power law graded materials are known to vary with distance from the surface.

Figure 3 shows the evolution of contact and separation processes during a full cycle of indentation. First column is locus of the contact at preload point, the second column shows the contact at pull-off point, the third column shows an arbitrary point after the pull-off point, and the last column demonstrates the deformation left after a full indentation cycle. Apparently, the contact area at preload is always the greatest for sample B-E12-VE50, while the sample B-E12 has the smallest contact area. The contact area for samples VE50 and P-VE50 are roughly comparable to that of sample B-E12-VE50 under the preload of 0.5 mN. However, difference between them starts to grow for higher preloads. Similar trends were observed for displacements.
δ at the preload point. Displacement at the preload is the largest for the sample B-E12-VE50 (≈14 μm for preload 0.5 mN). Samples VE50 and P-VE50 have almost equal displacement at preload values (≈10 μm for preload 0.5 mN), and the sample B-E12 under the same preload has considerably smaller value than that of other samples (≈6.8 μm). All these data suggests that the compliance of the new hybrid sample is the highest.

It is worth noting that, both bottom-view images and indentation data confirmed premature emergence of bending and buckling of the micropillars for sample B-E12-VE50. That is, the bending deformation for the micropillars, in control sample B-E12, usually takes place at preloads of ~25mN. However, for the new hybrid structure, we observed that the micropillars start to bend at the vicinity of 4mN preload. Hence, extraordinary compliance and preload dependence of the new hybrid structure can be attributed to facilitated bending and buckling of the base micropillars.

![Bottom-view images of the contact for samples](image)

We call this phenomenon shear-induced enhancement of compliance. The observed results advocates that there can be a set of extra shear forces acting on the top of the micropillars facilitating their bending and buckling. It is known that reversible buckling of the micropillars in film-terminated BFAs lead to enhancement of adhesion. In our new hybrid structure, the Poissonian deformation of the top viscoelastic layer, whether fully diffused in the underneath layer or not, likely induces stretching and consequently shear force on the elastic intermediate layer. Thus, the bending of the micropillars is strongly rendered in this sample comparing to the one without top viscoelastic layer. The possible mechanism of compliance enhancement is illustrated in Figure 4.
The new proposed adhesive structure benefits from adhesive mechanisms of both BFAs and PSAs. BFAs, theoretically, can increase adhesive strength and toughness of a flat control by enhancing the compliance and crack trapping. On the other hand, PSAs are capable of developing strong adhesive forces upon dissipation of the stored elastic energy through bulk deformation. In the hybrid structure, these mechanisms are coupled and create a strong yet durable adhesion. In summary, the biomimetic fibrillar interface functions as a spring foundation storing the elastic energy during the bonding. The stored energy in the pillars can be retrieved during the separation which facilitates the crack propagation at the interface instead of cohesive failure. The intermediate elastic layer facilitates integration of the viscous layer on top of the biomimetic fibrillar foundation and transfer the shear stress from the top to the base micropillars. The viscoelastic top layer dissipates a large amount of energy during the separation because of the bulk deformation and instabilities, which induced a shear stress at the interface and enhanced the bending and buckling of the fibril.

References

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Hamed Shahsavan and Boxin Zhao
Department of Chemical Engineering
Waterloo Institute for Nanotechnology
University of Waterloo
Ontario, Canada

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Biological Adhesive Systems

- Wet and fibrillar:
  - Maximized contact area
  - Enhanced interfacial toughness
  - Viscoelastis dissipation in separation
  - Capillary forces

- Dry and fibrillar:
  - Maximized contact area
  - Enhanced interfacial toughness
  - Frictional adhesion
  - Van der Waals forces

Biogistic Fibrillar Adhesives (BFA)

Mechanisms:
1. Tensile strength (graded elasticity)
2. Interfacial toughness (surface splitting)
3. Crack trapping (block propagation instabilities)
4. Enhancement of disentanglement (deformation of fibrils)

Design parameters:
1. Surface coverage
2. Tip shape
3. Hierarchy
4. Aspect ratio (height and diameter)

CommonTraditional Glues and Adhesives

- Inherent toughness of dry surfaces
- Full wetting and maximization of contact area
- Strong Adhesion

Separation:
- Crack propagation is hindered
- Filtration, fingering, and cavitation instabilities
- Possibility of cohesive failure and contamination

Topo Gecko Adhesive Pads

Properties:
1. Strong attachment/Great adhesion forces (1mm/s interface, vertical walls)
2. Anti-repeatability
3. Dry and self-cleaning (superhydrophobic, repeatable)
4. Material-independent (Van der Waals forces)
5. Anisotropic and smart

Adhesive strength vs Cohesive strength

Can we combine them?
Current Literature

1. Liquid/vapored BFA
   - Increment of pull-off and adhesion energy
   - Viscous loss and capillary force together
   - Winding cohesive failure of the viscoelastic material
   - Non-durable and wet!

2. Viscoelastic as the structural adhesive material
   - Increment of pull-off force and adhesion energy
   - Surface adaptation and viscous loss
   - Durability might be issue due to buckling or plastic deformation

3. Viscoelastic terminal layer
   - Increment of pull-off force and adhesion energy
   - Surface adaptation and viscous loss
   - Better durability comparing to PSA counterpart

**Functionally Graded Materials (FGM)

- Materials with gradient of mechanical properties (hard to soft)
- The greatest stress located on the stiffest part
- Resistance to surface damage and crack under harsh conditions

Proposed structure:

Most possible phenomena:

- Crack trapping and viscous dissipation at the terminal layer
- Separation instabilities in slip at bulk deformation
- Enhancement of compliant
- Enhancement of durability and structural integrity

Fabrication

SEM: Rheology and Indentation

**Results

Biomimetic Functionally Graded Adhesive

Pressure Sensitive Adhesives

Non-graded (VSB)

Chemically graded (VE50)

Gecko-inspired Adhesive

Geometrically graded (B-812)

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Optimization of Design

Effect of Intermediate Elastic Film Thickness

- Theoretically; energy release rate ~ t^-1
- Decrease in thickness increases the adhesion force
- Very thin layers show separation instabilities on top of the fibrils
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Rheological Studies

- Storage Modulus for: 100:1.6wt < 100:4wt < 100:10wt
- Loss modulus for:
  - 100:1.6wt > 100:4wt > 100:10wt
- tanδ(100:1.6wt) > tanδ(100:4wt) > tanδ(100:10wt)
- Viscous loss is greater for the softer PDMS

- The polymer releases very shortly after introduction of the stress.
- The holding time in indentation test must be higher than this value.
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13. Effect of Top Viscoelastic Film Thickness

- Variation of the thickness of the viscoelastic layer is not studied well.
- For flat viscoelastic samples slight increase.
- For our system, remarkable increment upon increase in thickness of viscoelastic layer.

**Thickest viscoelastic top layer!**

14. Load-Displacement Behaviour

- Vertical fibrillation, strain hardening for VE adhesives.
- Highest pull-off force for the new structure with thickest VE layer.
- Least slope change for new hybrid adhesive: limited deformation.

15. Visual Examination of Contact Formation and Break

- Greatest contact area for new hybrid adhesive.
- Greatest displacement at preload for new hybrid adhesive.
- Slight plastic deformation for new hybrid adhesive.

**The new hybrid structure is the most functional between the four!**

16. Sensitivity to Pressure (Preload)

- Higher preloads lead to larger contact areas.
- Reversible bending and buckling for control BFA sample occurs at 25mN.
- The pull-off force for sample B-E12-VE50 raises most pronouncedly after 3mN preload.
- Premature bending and buckling take place for sample B-E12-VE50 a 3mN.

Facilitated bending and buckling!

17. Shear-induced Compliance

1. The top viscoelastic polymer is diffused into the elastic intermediate layer: Top viscoelastic layer does not slip but deforms laterally.
2. The top viscoelastic layer is not diffused into the elastic intermediate layer: Top viscoelastic layer slips.

18. Conclusions

New hybrid structure benefits from:
- Higher pull-off force
- Higher adhesion energy
- Less bulk deformation
- Higher compliance and pressure sensitivity
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1) Crack growth patterns:
   - controlled by competition between two factors:
     - Interfacial crack propagation: Energy release rate \( G_c \)
     - Propensity of the bulk for deformation: Young’s Modulus \( E \)
   - Lower \( G_c/E \) → Interfacial crack propagation
   - Higher \( G_c/E \) → Bulk deformation (\( E \) → \( E' \))

2) Energy release rate for viscoelastic systems is more complex:

\[
G_c = G_c(1 + \phi \sigma) 
\]

Proportionality of damping factor to shift factor

\[
\phi \sigma \rightarrow \tan \delta
\]


3) Confinement ratio (a/h) also affects the pattern of crack propagation in linearly elastic or viscoelastic thin films

Higher a/h, more pronounced shear undulation

Determining ratio: \( \frac{G_c}{E} = \sigma \tan \delta \)

Nass et al. PRL, 2008

Properties of the terminal thin film appears to be most influential
Keeping $G_0$ constant during the tests and calculating:

- New hybrid structure is more prone to act like a liquid, experiencing more viscous loss.

Storage Modulus for:
- $100:4$ wt $< 100:10$ wt
- $100:4$ wt $> 100:10$ wt

Loss modulus for:
- $100:4$ wt $> 100:10$ wt

$\tan \delta_{100:4} > \tan \delta_{100:10}$

Viscous loss is greater for the softer PDMS.

Pull-off force against debonding speed showed similar behavior for both $100:10$ and $100:4$ samples:
1. $100:4$ is still in the elastic regime.
2. The debonding speed change range is limited.

Adhesion energy is higher for VE-T-24 indicating proneness of thicker viscoelastic films for dissipation of energy.

Adhesion energy vs debonding speed is almost constant as the $100:4$ PDMS mixture still is in an elastic regime.

Pressure sensitivity does not level off for the new hybrid samples. This can be attributed to pillars deformation.

Thicker $100:4$ terminal films show more sensitivity.

Very thin $100:4$ flat controls show no pronounced sensitivity.