Biologically Inspired Polymer Microfibers with Spatulate Tips as Repeatable Fibrillar Adhesives

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ABSTRACT. Being inspired by gecko foot-hairs, microfibers with flat spatulate tips are proposed as repeatable adhesives. They are fabricated by molding a master template fabricated using deep reactive ion etching and the notching effect. Fabricated polyurethane fiber arrays with 4.5 μm fiber and 9 μm tip diameter demonstrated macroscale adhesion pressures up to 18 N/cm^2 and overall work of adhesion up to 11 J/m^2 on a 6 mm diameter glass hemisphere for a preload pressure of 12 N/cm^2. These results show around 4 times higher adhesion and 5 times higher overall work of adhesion with compared to the flat polyurethane surface.

KEYWORDS. Fibrillar adhesives, microscale contact mechanics, compliant microstructures, biological adhesion.

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Geckos are exceptional in their ability to climb up smooth vertical surfaces because their hierarchical micro/nanoscale foot-hairs with their spatulate tips can attach to almost any smooth or micro/nanoscale rough surface repeatedly with a controllable adhesion pressure up to around 10 N/cm^2 (100 kPa)[1]. Recent findings have shown that van der Waals and possibly capillary forces play a dominant role in their fibrillar adhesion[1-4]. Many adhesion and contact mechanics models for the microfibrillar interfaces have been developed[5-10] and synthetic fibrillar adhesives have been attempted to be fabricated. Fabrication methods for recent micro/nanoscale synthetic dry adhesives consist of electron-beam lithography[11], replication of templates using molding or casting[12], drawing[13], printing[14], growing[18], and more complex microfabrication combined with self-assembly[15]. These works focused on fabricating micro/nanoscale high aspect ratio and high density polymer or carbon nanotube fibers on a flat substrate. However, these methods can not fabricate spatulate tips at the end of these fibers.

Flat and larger diameter spatulate tips are postulated to enhance the adhesion and work of adhesion significantly due to the increased tip contact area at the fiber-surface interface[5]. In order to model the work of adhesion enhancement approximately, a single polymer fiber is assumed to be stretched while its volume is conserved. In addition, if pull-off of each fiber tip is assumed to happen simultaneously where overall pull-off force per unit area is a constant value (c_1) and the elastic deformation is assumed to happen at the fiber stem only where the polymer Young's modulus (E) is assumed to be constant. Then, the maximum stretched length (x_c) and work of adhesion (W) of a single fiber during separation can be computed as

$$x_c = x_0 \frac{Ed_0^2}{Ed_0^2 - c_1 D^2} \qquad (1)$$

$$W = \int_{x_0}^{x_c} F dx = \pi E \frac{d_0^2 x_0}{4} \left[\frac{c_1 D^2}{Ed_0^2 - c_1 D^2} - \ln \frac{Ed_0^2}{Ed_0^2 - c_1 D^2} \right] \qquad (2)$$

where x_0 is the initial stem length, D is the fiber spatulate tip diameter, and d_0 is the fiber stem diameter. From (1) and (2), elastomer fibers with larger diameter tips elongate and dissipate energy significantly, and thus the work of adhesion per fiber is increased. Moreover, adhesion is also increased by a fiber array with larger flat spatulate tips since: (1) The fracture mechanics of the microfibers is flaw insensitive[19] (the stress at the interface is uniform and equal to the intrinsic adhesion strength at the instant of pull-off) and thus enables the maximum possible adhesion pressure; (2) Flat and compliant spatulate tips enable easier contact to a smooth surface with almost no alignment problem; (3) Fiber stretching enables larger number of fibers staying in contact with a smooth surface during pull-off. Therefore, this paper is focused on fabrication of polymer microfibers with flat and larger spatulate tips for fibrillar adhesives with improved adhesion capability.

The fabrication process of polymer microfibers with flat and larger diameter spatulate tips is explained in Fig. 1. A silicon-on-insulator (SOI) wafer (Addison Engineering) is used as a substrate which has 20 μm thick top silicon layer and 0.5 μm thick SiO_2 layer. After the optical lithography step in Fig. 1(a), the negative fiber array template is formed in Fig. 1(b). The required fiber profile shape is obtained in two steps. At first, isotropic etching is used for forming the circular supporting shape of the base of each fiber to reduce the stress concentration for preventing the fracture of fibers at their bases. Next, deep reactive ion etching (DRIE) is followed for forming vertical high

aspect ratio microchannels. Isotropic etching and DRIE were carried out consecutively in STS® Multiplex ICP RIE with 20 mT pressure, 130 sccm SF_6, 20 sccm O_2, 600 W coil power, and 120 W platen power. When the vertical etching reaches to the silicon oxide layer, it can not proceed vertically any more and then starts to expand laterally on the oxide interface. This effect is called the notching effect[17]. By controlling the lateral etching time, spatulate tip diameter is determined. Then, in Fig. 1(c), the template is filled with a liquid polymer under vacuum to remove not only the trapped air but also the native gas in the liquid polymer, and then the polymer is cured. Here, any polymer (e.g. Parylene® C) or any other fiber material can be also gas phase deposited inside to the template. In Fig. 1(d), the polymer fiber array with a backing layer is released by three step etching: At first, the bottom silicon layer is etched away by XeF_2 dry etching; Thin oxide layer is removed by buffered oxide etching (BOE); Finally, the 20 μm thick top silicon layer is etched away by XeF_2 etching in around 30 minutes to release the fibers with a backing layer. Here, the final etching step is critical. Since using a wet etching technique such as KOH etching would result in clumped fibers due to capillary forces during drying, XeF_2 dry etching is used to prevent any clumping issues. Moreover, since the DRIE process natively creates Teflon® like thin submicron film on the template microchannel side walls during the process[16], each released polymer fiber is expected to be coated with this hydrophobic thin film on their side walls (not at the spatulate tip surface). This very low surface energy coating could reduce the cohesion of microfibers significantly, and thus it could minimize any clumping during the mechanical contact of neighboring fibers.

Besides forming the flat spatulate tips, above fabrication process has other advantages with respect to previous fibrillar adhesive fabrication methods: (1) Fiber material can be fabricated from any polymer which can be in a liquid solution form or can be gas phase deposited; (2) Array of fibers can be fabricated in large areas up to 8 inch wafer size cost effectively using a single mask; (3) The yield is almost 100%; (4) This method can be extended to the fabrication of 100s of nanometer diameter fibers by using a higher resolution lithography step in Fig. 1(a), e.g. using phase masks. As the only drawback of this and all other previous methods, only vertical fibers can be fabricated while the biological foot-hairs mostly have an angle which enables an anisotropic friction property for the hairs[14]. Fabrication of angled microfibers with spatulate tips is a future work.

High tensile strength elastomer polyurethane (ST-1060, BJB Enterprise) with Young's modulus of around 3 MPa was selected as the fiber adhesive material. Scanning electron microscope (SEM) (Hitachi 2460N) image of the resulting microfiber array with 4.5 μm fiber diameter, 9 μm tip diameter, 4.5 μm base supporter diameter, 20 μm length, and 12 μm spacing between each fiber center (44% fiber tip area density) is displayed in Fig 2. These geometries are held by 80 sec isotropic etching for the fiber base supporter structures and by 21 min 20 sec vertical etching for the fiber and spatulate tips**.**

Performance of a fibrillar adhesive is characterized by its macroscale adhesion (P) and overall work of adhesion (W). To characterize these parameters for the fabricated fiber arrays during adhering to a glass hemisphere, a custom tensile macroscale adhesion measurement setup was built. Here, a glass hemisphere instead of a flat glass surface is selected as the test surface in order to have no alignment errors during the measurements.

A 6 mm diameter very smooth glass hemisphere (ISP Optics, QU-HS-6) attached to a load cell (Transducer Techniques, GSO-25) was moved vertically by a motorized stage (Newport, MFA-CC) with 100 nm resolution. The hemisphere was contacted to and retracted from the fiber array sample with a pre-specified preload force and a very slow speed (1 μm/s) to minimize any viscoelastic effects. The maximum tensile force during the glass hemisphere and fiber array separation (pull-off force) gave the adhesion, and the hysteresis area between the loading and unloading curves gave the dissipated energy between the loading and unloading of the fiber array. Dividing this dissipated energy by the maximum circular contact area during loading gave W^{10}. During the force measurements, an inverted microscope (Nikon Eclipse TE200) is used to measure the real circular maximum contact area between the hemisphere and the fiber array.

Adhesion and overall work of adhesion of 15x15 mm^2 area and 1 mm thick ST-1060 polyurethane fiber array samples and a 1 mm thick flat and smooth ST-1060 surface were measured on the glass hemisphere using the above setup. Here, the flat polyurethane surface was used as a control substrate to show the relative enhancement of P and W by structuring the same material as a cylindrical microfiber with flat spatulate tips. Since ST-1060 is also etched slightly during the final XeF_2 dry etching step in Fig 1(d), flat sample was also exposed to XeF_2 for about 30 minutes to have the same surface roughness with the flat spatulate tip surface.

Using the above setup, the fiber array and the glass hemisphere interface adhesion and overall work of adhesion are measured as shown in Fig. 3. Plots show the error bars measured from the force-distance data at two different locations on the fiber array for preloads up to 25 mN. Adhesion values saturate as preload increases, and the array of

fibers has around 4 times higher adhesion than the flat surface. Dividing the adhesion to the optically measured maximum circular contact area during loading, maximum adhesion pressure for the fiber array can be computed as 18 N/cm^2 at a preload pressure of 12 N/cm^2. Overall work of adhesion of the fibers is 5 times higher than the one from the flat elastomer surface. This energy dissipation enhancement is due to the lost energy during separating the elastic and highly stretched fibers from the adhered glass surface as given in (2). ST-1060 fibers stretched up to 500% strain in the experiments (observed by profile view optical imaging) which would show the reason of the enhancement of the elastic energy loss during unloading the fibers.

Macroscale adhesion data from the fiber array in this work are compared with the previous works as given in Table 1. The polymer fibers with spatulate tips show better adhesion pressure than other synthetic gecko inspired fibrillar adhesives with no spatulate tips although the single fiber in this work is over 20 times thicker than the single fibers which are fabricated in other works. In order to even increase the adhesion performance in this work, microfibers with tips will be scaled down to 100s of nanometers in diameter using phase mask type of sub-micron lithography techniques. Here, N times self-similar scaling down in fiber diameter will generate $\sqrt{N}$ times higher adhesion[20], and smaller fibers will need less preload than larger fibers to obtain the same adhesion.

In conclusion, polyurethane elastomer microfiber arrays with flat spatulate tips are proposed as biologically inspired repeatable fibrillar adhesives in this work. For a preload pressure of around 12 N/cm^2, adhesion pressures up to 18 N/cm^2 and overall work of adhesion up to 11 J/m^2 are demonstrated for polyurethane fibers with 4.5 μm fiber diameter, 9 μm tip diameter, 20 μm length, and 44% fiber tip area density on a 6

mm diameter glass hemisphere. These repeatable fibrillar adhesives would have wide range of applications as space, biomedical, sports, etc. adhesives.

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TABLE CAPTIONS

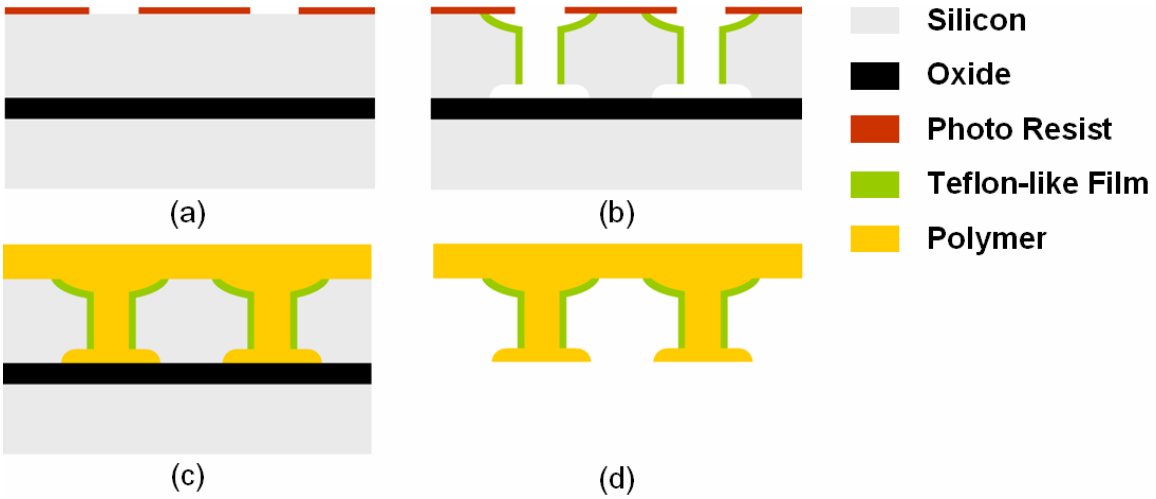
Table 1. Comparison of adhesive strength among various natural and synthetic gecko inspired micro/nanofibers[18].

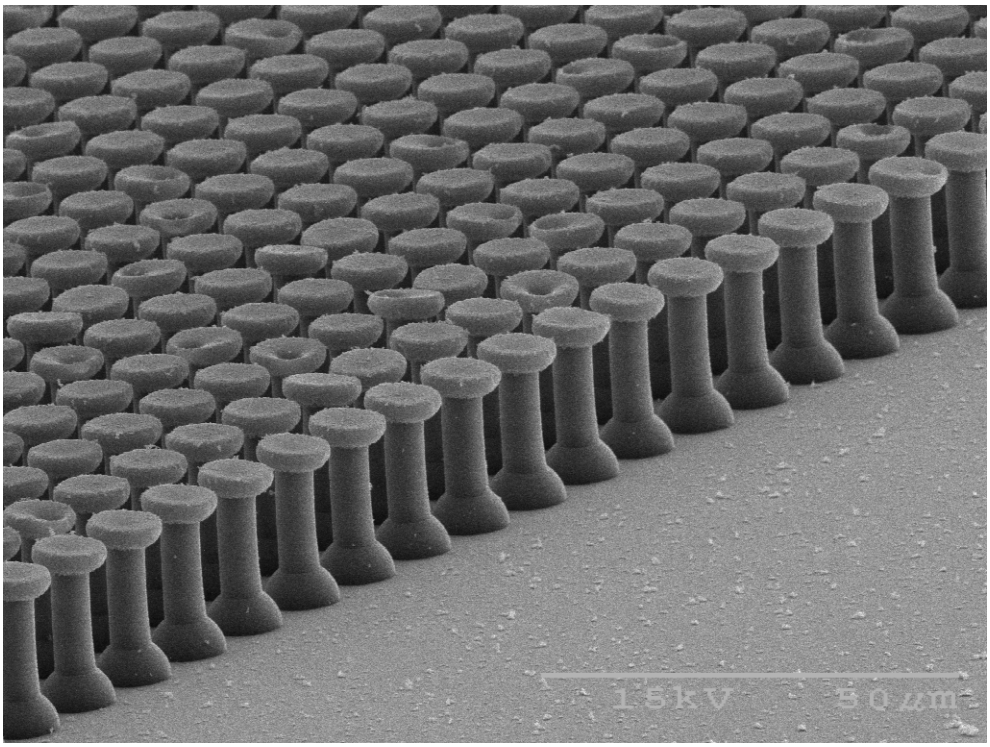
FIGURE CAPTIONS

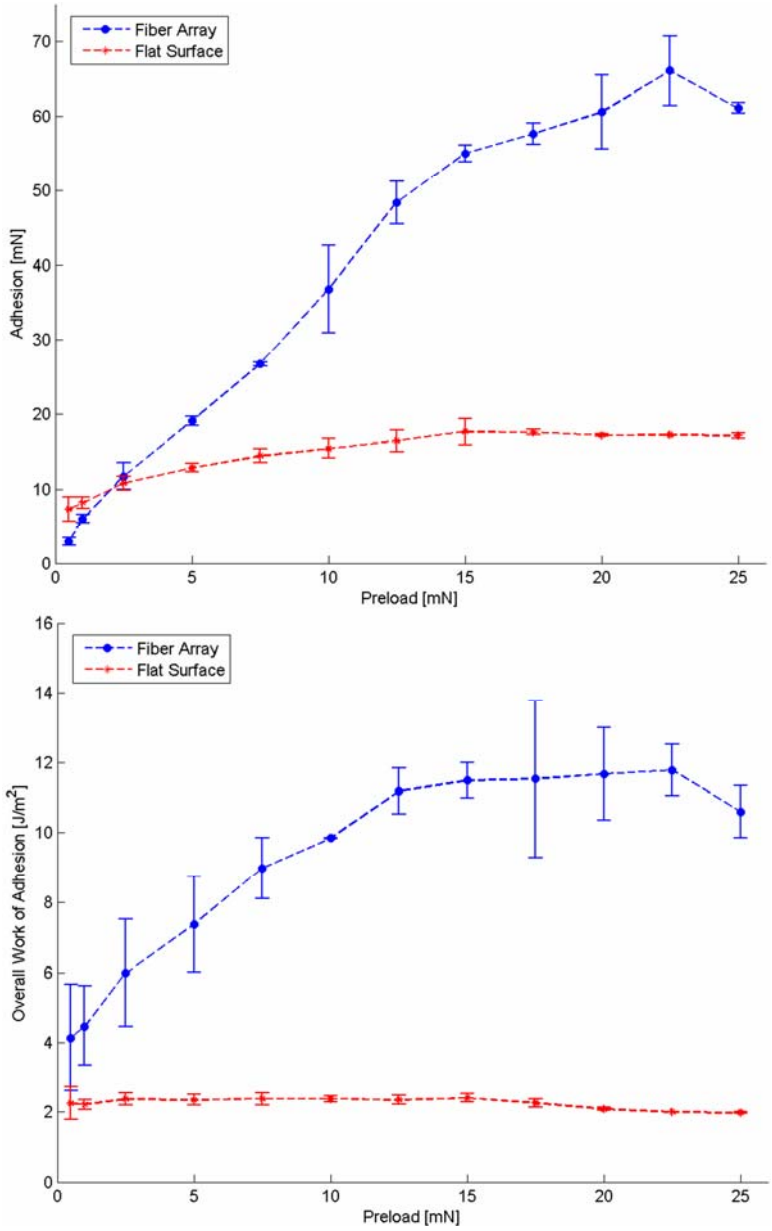
FIG. 1. Schematic process flow steps for the fabrication of polymer microfiber arrays with flat spatulate tips: (a) An SOI wafer top surface is patterned using optical lithography; (b) Negative fiber array template is formed using a two-step deep reactive ion etching process; (c) The template is filled with a liquid polymer under vacuum and the polymer is cured, or it is filled by gas phase deposition of a polymer; (d) Polymer fiber arrays with spatulate tips and a backing layer are released.

FIG. 2. SEM image of the isometric view of a polyurethane elastomer microfiber array with 4.5 μm fiber diameter, 9 μm tip diameter, 20 μm length, and 44% fiber density (Scale bar: 50 μm).

FIG. 3. Macroscale adhesion (upper plot) and overall work of adhesion (lower plot) of polyurethane microfibers and flat polyurethane flat control surface on a 6 mm diameter glass hemisphere for varying preloads.


(a)
(b)
(c)
(d)
Silicon
Oxide
Photo Resist
Teflon-like Film
Polymer


15kV 50µm


Fiber Array
Flat Surface
Adhesion [mN]
Preload [mN]
Fiber Array
Flat Surface
Overall Work of Adhesion [J/m²]
Preload [mN]