Spider Silk Inspired Functional Microthreads
Vasav Sahni, Disha V. Labhasetwar, and Ali Dhinojwala*

Department of Polymer Science, Integrated Bioscience Program, The University of Akron, Akron, Ohio 44325-3909, United States

Supporting Information

ABSTRACT: We employ the adhesive web building strategy used by modern orb-weaving spiders to produce functional microthreads that are similar in structure (beads-on-a-string (BOAS) morphology) and adhesive properties to the capture-silk threads of the spider web. The diameter and spacing of droplets (beads) are controlled by varying the viscosity, velocity, and surface tension of the coating fluid. Using these functional threads, we also describe the behavior of the BOAS morphology during contact (mimicking the collision of an insect with the web) and during separation (mimicking insect rescue from the web). Our results show that the BOAS structure performs better than a cylindrical structure for adhesion, which may explain why this morphology is so prevalent in spider webs despite the cost of increasing the visibility of the web.

INTRODUCTION

Spiders display innovative behavioral strategies in conjunction with micrometer-size custom-made adhesive silk threads incorporated into prey capture webs.1 The proteins as well as low-molecular-mass organic and inorganic materials used in these webs evolved over millions of years into a class of natural adhesives with outstanding properties. Multiple types of adhesives are often used in a single spider web; however, the adhesives used to capture prey have received the most attention. Silk threads spun by modern orb-weaving spiders to capture prey consist of a beads-on-a-string (BOAS)-like morphology, where the beads of glue are composed of adhesive polymeric glycoproteins3−5 and low-molecular-weight hydroscopic compounds.6 The string is composed of a pair of soft and highly extensible viscoelastic axial silk fibers.7 The BOAS threads are produced from triads of spigots that lie on the posterior spinnerets of spiders. Each triad is composed of a gland that produces an axial silk fiber (flagelliform gland), two glands that secrete glue (aggregate gland), and their respective spigots. The spigot from the fiber gland is arranged between the spigots of the glue glands such that the glue and fibers are simultaneously extruded8 and glue coats the fiber. The composition of the glue, its physical characteristics, and the spinning conditions of the silk produce an initially cylindrical coating of the glue on the axial silk, which breaks down into an equally spaced micrometer-sized array of glue droplets due to Rayleigh instability. After a period of time, the glue droplets become more viscous and develop elasticity, which become important in enhancing adhesion.5

Interestingly, even though Rayleigh instability results in reducing the exposed surface area (in the absence of no external forces that may cause deformation of the droplets) of the adhesive coating, the BOAS structure is prevalent. In addition, the BOAS thread is more visible than the cylindrical thread—an undesirable characteristic in a trap. The success of BOAS morphology is also evident through other examples, especially by its presence in the gumfoot silk threads9 spun by the cobweb-weaving spiders, the evolutionary descendents of modern orb-weaving spiders.

Here, we employ the strategy utilized by modern orb-weaving spiders to produce functional microthreads (hereafter referred to as “functional threads”). We also tune the magnitude of functionality imparted by varying the velocity, viscosity, and surface tension of the coating material. In general, higher viscosity and velocity and lower surface tension of the fluid result in the formation of bigger and farther-spaced droplets. Using these functional threads, we describe the behavior of the BOAS and cylindrical morphologies during contact (mimicking collision of an insect) and during separation (mimicking insect rescue) and show that the BOAS structure is better suited than a cylindrical structure for adhesion, despite higher visibility of the adhesive thread in the web.

EXPERIMENTAL SECTION

Preparation of Functional Threads. Nylon fibers (gifted by Goodyear, Akron, OH) of diameter 30 μm were vertically withdrawn, at a controlled velocity, from a reservoir filled with poly(dimethylsiloxane) (PDMS) (equal parts of Sylgard 528A and B provided by Dow Corning). The cylindrical coating of PDMS spontaneously breaks into an array of droplets. The thread is placed in a vacuum oven at 80 °C for 2 h to cure the PDMS. To show the effect of viscosity on drop dimensions and spacing, un-cross-linked PDMS of kinematic viscosities 10 cst, 100 cst, and 1000 cst (10−3 m2/sec, 10−4 m2/sec, and 10−5 m2/sec, respectively) were used (Dow Corning).

Measurement of Adhesion Force. Sixteen-millimeter samples of the cured threads, mounted across the gap of a U-shaped cardboard piece, were clamped onto the top grip of NanoBionix (Agilent Tech., formerly MTS) as shown in Figure S1 (Supporting Information). A 2 mm-wide clean glass plate was clamped onto the bottom grip. The cylindrical coating of the glue on the axial silk piece, were clamped onto the top grip of NanoBionix (Agilent Tech., formerly MTS) as shown in Figure S1 (Supporting Information). A 2 mm-wide clean glass plate was clamped onto the bottom grip. The thread is pushed onto the glass plate to a force of 20 μN at a rate of...
0.1 mm s$^{-1}$ (displacement-controlled loading), held there for 60 s, and then pulled away from the substrate at a fixed rate (2 mm/s for Figure 2c,d, and 0.5 mm/s and 2 mm/s for Figure 3, inset), while the force-displacement response is recorded (Figure S2). Force is measured by the displacement of the actuating transducer in the NanoBionix. The maximum displacement of the transducer is ±1 mm. The force registered just before the thread releases contact with the class plate is recorded as the adhesion force. Ten samples were tested three times each. Values are plotted as mean ± SD from 30 measurements each.

**Measurement of the Tensile Properties.** Independent tensile tests on the threads were performed, by clamping a thread onto the top and bottom grips of the NanoBionix, to find out the strain energy stored (area under the stress–strain curve) when the thread is stretched (Figure S3). The maximum strain to determine the energy stored in the thread was determined from the maximum strain experienced by the thread during the adhesion measurements. These tensile tests were performed at the same stretching rates that the threads experienced during adhesion measurements, to account for any viscoelastic effects. Strain energy values were determined from testing ten 16-mm long thread samples. The equation used to calculate the contribution of the energy stored in stretching the thread is discussed in the main text.

### RESULTS AND DISCUSSION

A continuous microfiber (Nylon) is pulled vertically out of a reservoir containing PDMS at different velocities. We choose PDMS as the liquid because it has low surface tension, and the effect of gravity on the droplets is negligible (bond number ≪1). Depending on the capillary number, $Ca$, the cylindrical coating breaks down into an array of droplets due to Rayleigh instability. The coated fiber is then cured by heating at 80 °C to stabilize and immobilize the droplets. Figure 1a,b shows a capture thread spun by *Argiope trifasciata* and functional threads formed by coating nylon fiber with PDMS.

The adhesion of the fibers can be easily tuned by varying the capillary number. Upon withdrawing a fiber from the reservoir, the thickness of the entrained cylindrical film, $\varepsilon$, for bond number ≪1 (which is the case here), is given by the following equations:

$$
\varepsilon = \begin{cases} 
1.34dCa^{2/3}, & Ca \ll 1 \\
\frac{1.34dCa^{2/3}}{1 - 1.34Ca^{2/3}}, & Ca \sim 1 
\end{cases}
$$

(1)

Here, $Ca = \eta \gamma / \sigma$ and $d$, $\eta$, $\gamma$, and $V$ are the radius (of the uncoated fiber), viscosity, surface tension, and velocity of the coating, respectively. Plateau$^{11}$ and Rayleigh$^{12}$ showed that the initially cylindrical coating breaks into an array of drops such that the wavelength of the array, $\lambda$, as well as the radius of the sphere, $R$, are both dependent on the thickness of the cylindrical coating $\varepsilon$.

$$
\lambda > 2\pi(d + \varepsilon) 
$$

(2)

$$
R = \left[\frac{3\lambda}{4}((d + \varepsilon)^2 - d^2)^{1/3}
$$

(3)

In essence, by varying $\eta$, $\gamma$, or $V$, one can change $Ca$. Changing $Ca$ will change the thickness of the coating and hence the radius of the cylinder, which will determine the wavelength $\lambda$ of the array of spheres of radius $R$. Using this principle, the size and spacing of the drops on the functional threads were tuned by varying the capillary number. Figure 1c shows the effect of velocity, $V$, on the size and the spacing of the drops. The volume of the drop as well as the spacing between the droplets increases with increasing velocity of the coating. Figure 1d shows the effect of viscosity, $\eta$, of the coating on the volume and the wavelength of the droplets. Similar to the velocity, increasing the viscosity also results in higher drop volume and longer wavelength.
The modern orb-weavers have developed an intriguing structure for their capture threads, utilizing glue droplets as adhesive beads on a very elastic silk thread. The glue droplets behave like viscoelastic solids and can withstand large extension as shown in Figure 2a. The “suspension bridge”-like structure increases the peeling force and makes the capture threads very sticky. This was one of the reasons we chose to use PDMS as the fluid to mimic this morphology, as cross-linked PDMS is elastic and stretchy. Figure 2b shows an optical image of the functional thread as it is peeled off the surface. Similar to the capture silk threads produced by spiders, a suspension bridge-like structure is observed in the functional thread (Figure 2b). The adhesion forces required to peel the functional threads are shown in Figure 2c. Higher capillary number was accompanied by higher force of adhesion. Interestingly, capture silk threads spun by different orb-weaving spiders also show similar behavior: generally, capture threads with bigger and farther-spaced drops demonstrate higher adhesion.

It has been shown that the force of adhesion depends on the mechanical properties of both the fiber and the glue droplets. The contributions from the fiber and the glue can be separated by using a recently developed energy model. The work performed to pull a thread off a surface is consumed in stretching of the axial fiber and the energy required to peel the droplets from the surface. Figure S1 shows a sketch defining the variables used in the energy model. The total work on the system ($W_t$) is calculated by integrating the product of the force $f(h)$ times the infinitesimal height change $dh$ from $h$ to $h + dh$.

$$W_t = \int_{(h=0)}^{(h=h_f)} f(h) \, dh$$ (4)

The strain energy stored in the thread when it is pulled from its initial position until it separates from the surface, $U_{\text{strain}}$, is given by the following equation:

$$U_{\text{strain}} = \int_{(\varepsilon=0)}^{(\varepsilon=\varepsilon_f)} \sigma(\varepsilon) \, d\varepsilon$$ (5)

$\sigma(\varepsilon)$ is the value of load at displacement $\varepsilon$, as measured from independent tensile tests. Here, the assumption is that the length of thread adhered to the substrate at any time during the adhesion measurement is negligible compared to the total length of the thread, which is reasonable since the width of the substrate (2 mm) is much less than the length of the thread (16 mm). Subtracting eq 5 from eq 4 gives the energy required to separate the glue drops from the surface, $U_{\text{glue}}$. Figure 2d shows the energy of adhesion of the glue drops as a function of the capillary number. The increase in the energy of adhesion of the glue drops with increasing capillary number, indicating that the increase in force of adhesion is due to the glue drops and not to the difference in tensile properties of the thread. The extent of functionality (adhesiveness in this case) imparted to a fiber can thus be easily tuned by varying the capillary number.

Interestingly, when a newly spun capture silk thread (the glue coating is still cylindrical) spun by *Larinioides cornutus* is brought into contact with a clean glass plate and then separated from it, the force of adhesion measured at separation is around 3 times lower than when the glue coating has broken into an array of droplets (Figure 3, inset). The difference in adhesive forces can be attributed to higher contact area established by the glue droplets than the glue cylindrical morphology and the higher energy dissipated in separating the glue droplets than in separating the glue cylinder, since peeling glue droplets from a surface will have multiple crack-initiation, crack-propagation, and crack-arrest events, whereas peeling a cylinder will require only one of each. Using the functional threads as an example, we studied the effect of these factors (interfacial contact area established and energy dissipation during separation) on the
adhesion of both morphologies (cylinders and spheres) in an attempt to understand the advantage of the BOAS morphology on the capture silk threads.\(^{(15)}\)

Considering a linear elastic model, we can calculate the differences in contact areas between the BOAS morphology and the cylindrical coating of similar volume (mimicking insect capture). For the sake of simplicity, we assume the glue drops to be spherical. (In reality, the glue drops produced by spiders are paraboloidal.) According to the Johnson–Kendall–Roberts (JKR) theory, the contact radius, \(a\), of the circle formed by pressing a deformable sphere onto a rigid flat surface is given by\(^{(16)}\)

\[
a^3 = \frac{R}{K}(P + 3\pi WR + \sqrt{(6\pi WR P + (3\pi WR)^2)})
\]

(6)

In the JKR model, \(P\) is the applied load, \(R\) is the radius of curvature of the sphere, \(W\) is the adhesion energy of the sphere with the substrate, and \(K\) is related to the effective elastic modulus (\(E_{eff}, K = 4E_{eff}/3\)). In the case of the cylindrical thread, a contact rectangle of length, \(2l\), and width, \(2b\), is formed upon pressing a deformable cylinder on a rigid flat surface and is given by\(^{(17)}\)

\[
\frac{3\pi b^{1.5}}{8} = \frac{P}{Klb^{0.5}} + \sqrt{\frac{6\pi W}{K}}
\]

(7)

Here, \(S\) is the radius of the cylinder, and other terms are similar to those described in eq 5. Figure 3 compares the interfacial area, calculated assuming JKR contact, established by a cylinder and the eventually formed spheres, with a rigid flat substrate. Since the cylinder breaks into an array of spheres, the volume of the sphere is equal to the volume of one wavelength of cylinder. For the same loading force, a sphere establishes higher contact area than a cylinder of equal volume (Figure 3). (Details of these calculations are given in the Supporting Information.) The glue coatings produced by orb-weaving spiders, as well as the cross-linked PDMS coating on the functional threads, exhibit elasticity, and the elastic model in these calculations is used to illustrate that the sphere geometry (BOAS threads) results in higher contact area with the substrate.

In addition to the higher surface area established by the array of spheres, the BOAS morphology adopted by spiders also has a higher force required to separate the array of spheres from a surface (mimicking insect rescue). The higher separation force is due to the multiple crack-initiation, crack-propagation, and crack-arrest events as opposed to a single event when a cylinder is separated from a surface. Kendall\(^{(18)}\) has showed that different interfaces between materials of different thicknesses have a considerable effect on crack propagation: when a crack meets a thicker material, it experiences transient retardation, whereas when a crack meets a thinner material, it experiences transient acceleration. Hence, periodic structures (like spider capture silk and functional threads) substantially increase static interfacial fracture energy through arresting cracks at a thicker interface. Moreover, the dynamic interfacial fracture energy, i.e., resistance to a moving crack, is also raised due to fluctuations of crack speed at a number of periodically spaced interfaces. Kendall’s analysis on peeling tapes suggests that the spacing and diameter of the glue drops are important in increasing the peeling force. We illustrated the importance of this hypothesis by referring to the works of Ghatak and Chaudhury.\(^{(19)}\) For the sake of simplicity, the array of drops can be roughly approximated as a one-dimensional adhesive film having equi-spaced incisions on it (distance between incisions = \(s\)). For separating a smooth surface of a
finite flexural rigidity $D$, the stress decay length, $κ^{-1}$, is given by\textsuperscript{19}

$$κ^{-1} = \left( \frac{Dw^3}{12\mu} \right)^{1/6}$$

(8)

Here, $D = 0.02$ N m, $\mu = 1$ MPa, and $w$ was taken to equal the width of a single glue droplet, while $s$ was taken as the wavelength of the droplets (details in the Supporting Information). For the dimension of the array shown in Figure 3, $sκ$ (a dimensionless parameter defined in ref 17, which describes the thickness and the wavelength of the array), for the array of beads varies from 0.3 to 1.3, while separating a cylinder from the same surface would have $sκ = \infty$. It has been shown that energy required to separate the film reduces as $sκ$ increases,\textsuperscript{19} which implies that the energy required to separate a BOAS thread will be higher than that required to separate a cylindrical thread. Higher energy dissipated while separating a BOAS thread, together with the higher interfacial surface area established by the BOAS morphology demonstrates that the BOAS structure exhibits higher adhesion than the cylindrical structure.

**CONCLUSION**

In summary, we have mimicked the strategy used by orb-weavers to develop functional microthreads with excellent adhesive properties. By varying the capillary number, the structure and morphology of the functional threads can be controlled. The simplicity and scalability of this method over conventional methods used to produce such structures—template-based synthesis,\textsuperscript{20} vapor-phase synthesis,\textsuperscript{21} solution-phase deposition,\textsuperscript{22} and coaxial electrospinning\textsuperscript{23}—allows rapid and easy large-scale fabrication of one-dimensional BOAS structures with a wide range of compatible component materials. The BOAS structure establishes higher interfacial contact area than a cylindrical morphology for the same applied load. Also, the energy required to separate a BOAS thread is higher on account of multiple crack-initiation, crack-propagation, and crack-arrest events. These results demonstrate that the BOAS structure has higher adhesion than a cylindrical morphology, which may explain why the BOAS morphology is seen in multiple species of spider and over evolutionary history.

**ASSOCIATED CONTENT**

Supporting Information
Details of calculations of interfacial contact area, the schematic of the experimental setup, typical force–distance curve during an adhesion measurement, and a typical tensile test data for BOAS. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author
*E-mail: ali4@uakron.edu.

**ACKNOWLEDGMENTS**

This work was supported by the National Science Foundation. We also acknowledge the financial support of the Austen Bioinnovation Institute in Akron (ABIA).

**REFERENCES**

(5) Sahni, V.; Blackledge, T. A.; Dhinojwala, A. Nat. Commun. 2010, DOI: 10.1038/ncomms1019.
(13) For the sake of simplicity, in expressing a relation between the thickness of the cylinder and the dimension of the drop formed, the assumptions made here are that the drops are spherical and that there is no fluid “bridge” between two drops. In reality, however, the drops formed are paraboloidal (if the fluid wets the fiber), and a cylindrical film of thickness is much less than the thickness of the initial cylinder bridges between two drops.
(15) Interestingly, all of the difference in force of adhesion in actual spider capture silk cannot be attributed to the difference in morphology because, in capture silk thread, the glue, after being coated onto the silk fibers, undergoes cross-linking\textsuperscript{2} to stabilize and immobilize the glue droplets onto the silk fibers. This contrasts the situation when the glue is still cylindrical and the glue is not cross-linked. Nonetheless, morphology of the glue drops plays a significant role in influencing the adhesive capabilities of the capture threads.
(22) Milliron, D. J.; Hughes, S. M.; Cui, Y.; Manna, L.; Li, J. B.; Wang, L. W.; Alivisatos, A. P. Nature 2004, 430, 190.