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Short communication

Physical characterization of the liquid adhesive from orb-weaving spiders

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ABSTRACT

Orb-weaving spiders produce bioadhesives that are used to capture their prey. In this paper, the physical properties of these adhesives are characterised. The liquid adhesive from *Argiope argentata* spiders has been studied and the morphological properties of the droplets, including size, shape and volume were determined. An estimation of viscosity and Young's modulus using atomic force microscopy has also been carried out. Morphological characterization confirmed that the liquid adhesive displayed a typical beads-on-a-string (BOAS) morphology on the silk fibres. The experimental data confirmed that the elastic modulus of the liquid adhesive from *A. argentata* was in the range 20–100 kPa which is in agreement with the Dahlquist criterion for adhesives.

1. Introduction

Orb-weaving spiders produce several types of silks, each of which has a specific functional role. For instance, drag line silk produced by the major ampullate glands makes the radii of the orb-web. The orb-web must be able to cope with the kinetic energy of flying insects that arrive on it. The mechanical properties of spider silk such as tensile strength and extensibility determine the behaviour of orb-webs.

Orb-weaving spiders use a special thread coated with an aqueous adhesive to capture their prey. This kind of thread is known as viscid thread and it is produced together with the aqueous adhesive by three spigots. The thread is spun in the flagelliform gland after which it is coated with the adhesive produced in the aggregate glands [1]. Volrath et al. [2] have investigated the chemical composition of the water soluble fraction of this aqueous adhesive. They found hygroscopic components related to neurotransmitters such as GAB-amide, choline, lysine, serine, etc. Tillinghast [3] and Sahni et al. [4] were able to analyse the non-soluble fraction of the adhesive. The presence of galactosamina, galactose, mannose, glucosamine, fucose and glucose would indicate that glycoproteins are responsible for the stickiness of this adhesive as they are the only components with long branches.

Foelix [5] and Edmonds et al. [6] have reported that when the viscid thread is coated with the adhesive, the glue covers it evenly but it tends to form droplets due to Rayleigh instability, displaying a beads-on-a-string (BOAS) morphology [7–13]. Opell and Hendricks [14] have performed drop adhesion measurements. They stretched single adhesive drops until separation from a glass probe. The maximum adhesion forces they found were in the order 0.1–0.4 mN. Sahni et al. [4] carried out load–relaxation tests. The forces they measured were around 0.2 mN. They also discussed the rheology of adhesive drops. They claimed that such drops behave neither as a viscous liquid nor as a viscoelastic liquid. Instead, the adhesive drops exhibit the characteristics of a viscoelastic solid.

The studies previously published in the literature assessed the chemical and mechanical properties of the spider adhesive. However, in order to fully understand the physics of the adhesion of spider glue, other properties must be studied. One of the basic rules of adhesion is that one of the surfaces to be adhered should be relatively soft. It has been shown that the elastic modulus of the components strongly influences adhesion in biological systems [15]. In this paper, we give an estimation of other physical properties of the spider adhesive glue such as surface area, contact angle, viscosity and Young's modulus.

2. Experimental section

2.1. Materials

Argiope argentata (Fabricius, 1775) spiders, an American species of the Araneidae family, were used in this study. Female adult spiders of 3.5–5 mm in prosoma width were collected in the outskirts of Lima, Peru. They were housed in 30 × 20 × 10 cm cages and were fed larval stage mealworms (*Tenebrio molitor*) three times per week. Cardboard frames with a rectangular opening were used to collect viscid silk samples. The ends of the silk samples were glued to the frames so that a part of the sample remained untouched. Silk samples were collected from the webs of three different spiders. At least three webs from each spider were used.

2.2. Characterization techniques

Micrographs of the viscid silk were taken in a FEI-QUANTA 200 scanning electron microscope (SEM) in low vacuum with a voltage in the

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range of 20–30 kV with a working distance of 10 mm. Three different silk samples were viewed directly without drying and without conductive coating. At least four SEM micrographs were taken from each specimen. This allowed for the measurement of sixty different drops.

Nanoindentation tests were performed in a Nanosurf Easy Scan atomic force microscope (AFM) at 25 °C and 80% RH. A monolithic silicon NanoWorld Pointprobe® probe with a spring constant of 0.17 N/m was used. The tip radius of the probe is around 8 nm and its half cone angle is 50°. Mica TO-220 was used as substrate. Samples were tested immediately after being collected. Three samples were used. Each indentation test was repeated 5 times. The duration of each test was 1 s.

2.3. Young's modulus estimation

The indentation tests were repeated 5 times for each point. The average values were used to plot the curve of the cantilever deflection against the height of the sample.

If we consider an infinitely stiff tip and a soft flat sample, the Hertz model can be used to predict the relation between indentation and loading force [16–18]. The Young's modulus can be estimated by following Eq. (1):

$$z - z_0 = d - d_0 + \sqrt{\frac{k}{\left(\pi/_2\right)\left[E/_{(1-\nu^2)}\right]\tan(\alpha)}}\sqrt{d - d_0}. \tag{1}$$

Where E is the Young's modulus, ν is the Poisson ratio (taken as 0.5 corresponding to an incompressible material), k is the spring constant of the cantilever (0.28 N/m), α is the opening angle of the cone (50°), z is the height of the sample and d is the deflection of the cantilever. The 0 subscript accounts for the offset values.

3. Results and discussion

Fig. 1 shows a SEM image of the spider adhesive glue forming drops on the spider silk thread. This image resembles other examples of the well described beads-on-a-string (BOAS) morphology. The BOAS phenomenon can be observed while pulling apart a thin film of a viscoelastic fluid such as saliva, fish slime, cellular protoplasm, etc. [19]. It can also be observed when blending incompatible polymers in the melt state. During shear flow, these polymers are extended into long threads, but when the flow stops, the external thread breaks up into small droplets [20].

Fig. 2 shows a schematic representation of the BOAS morphology. According to Sahni et al. [21], when the threads come out of the spider spigot, the axial silk thread is coated by a regular cylindrical layer of glue. The glue layer then breaks down into an equally spaced array of droplets due to Rayleigh instability.

For the adhesive droplets studied here, we have used some of the equations that describe the BOAS phenomenon to assess the physical characteristics of the spider glue from *A. argentata*. Sahni et al. [21] have related the thickness of the glue cylinder (e), the wavelength of the array of drops (λ) and the radius of the uncoated fibre (d) by using Eq. (2):

$$\mathrm{R} = \left[(3\lambda/4)\left((\mathrm{d}+\mathrm{e})^2 - \mathrm{d}^2\right)\right]^{1/3}. \tag{2}$$

Image analysis was used to measure the radius of the drops (R), the wavelength and the 'd + e' length. The average values obtained for these parameters were 6.5 μm, 111.2 μm and 1.3 μm, respectively. Then, according to Eq. (2) the thickness of the glue coating is around 0.37 μm and the radius of the uncoated fibre is 0.93 μm.

The equation proposed by Ryck and Quéré [22] for the capillary number when withdrawing a fibre from a reservoir (3) is:

$$\mathrm{e} = 1.34\ \mathrm{d}\ \mathrm{Ca}^{2/3},\ \ \mathrm{Ca} \ll 1. \tag{3}$$

The Capillary number being:

$$\mathrm{Ca} = \eta \mathrm{V}/\gamma. \tag{4}$$

Where η, V, and γ are the viscosity, velocity of the coating and surface tension.

From Eq. (3), the value of Ca is 0.228. Eq. (4) relates the surface tension of the droplets with the coating velocity and the fluid viscosity. Volrath et al. [23] have estimated the reeling velocity of spider silk at around 20 $\mathrm{mm \cdot s^{-1}}$. However, as far as the authors are concerned, there are no published data for the viscosity of the spider adhesives. Common values for the surface tension of other polymer solutions range 30×10^{-3}–60×10^{-3} $\mathrm{Nm^{-1}}$ [24–26]. Considering these surface tension values, the viscosity of the spider glue should be in the range 340–680 Pa·s.

For the sake of simplicity, Fig. 2 shows spherical drops. However, in order to estimate the contact angle, a different approach must be used. When a liquid is placed on a flat solid surface it will form a drop with a specific contact angle between the liquid and solid phases. By contrast, when the solid phase is a fibre the liquid forms a surface of revolution as shown in Fig. 3. Within the framework of Laplace's formula of surface tension and Young's equation of wetting, Carroll [27] has studied the wetting properties of fluids on fibre surfaces. Fig. 3 depicts the analysis of Carroll [27] for the static shape of a droplet on a fibre neglecting the effect of gravity. Carroll proposed a method for estimating the contact angle of a drop-on-fibre system. This method uses two dimensionless

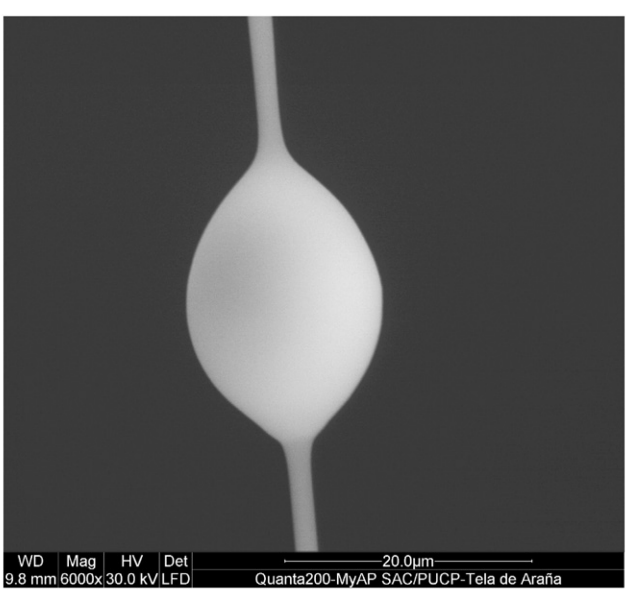

Fig. 1. SEM micrograph of viscid silk showing the typical beads-on-a-string (BOAS) morphology of the adhesive droplets on the silk fibres.

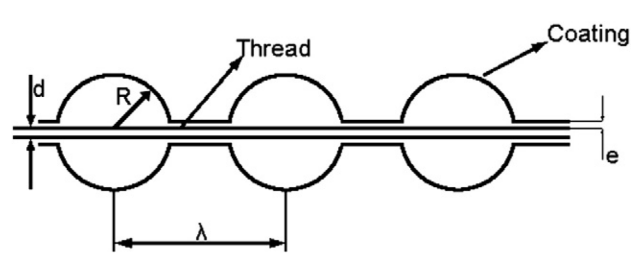

Fig. 2. Typical representation of the beads on a string (BOAS) morphology for the droplets of adhesive on a thread.