



Revising the exceptionally high thermal diffusivity of spider silk



Raquel Fuente, Arantza Mendioroz, Agustín Salazar*

Departamento de Física Aplicada I, Escuela Técnica Superior de Ingeniería, Universidad del País Vasco UPV/EHU, Alameda Urquijo s/n, 48013 Bilbao, Spain

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ABSTRACT

The outstanding mechanical properties of spider silk have been widely studied, but measuring its thermal transport properties is actually a challenge, since the silk fibers are very thin (few micrometers in diameter). Recently, an exceptionally high thermal diffusivity value for the dragline silk has been reported, $70 \text{ mm}^2 \text{ s}^{-1}$, similar to the best thermal conducting metals. In this work, by means of a lock-in thermography setup specially designed to measure thermal diffusivity of very thin filaments, we have measured the thermal diffusivity of spider dragline silk. The value we have obtained, $0.20 \pm 0.01 \text{ mm}^2 \text{ s}^{-1}$, is 400 times lower than the previously reported result and falls within the typical diffusivity range of biomaterials ($0.1\text{--}0.3 \text{ mm}^2 \text{ s}^{-1}$).

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1. Introduction

Spider silk is a fibrous biomaterial which consists almost entirely of large proteins. It shows outstanding mechanical properties combining high mechanical strength and elasticity. Over the years, several works analyzing the intricate internal structure of the silk and relating it to its exceptional mechanical properties have been published [1–3]. Besides, spider silk is also antimicrobial, hypoallergenic and completely biodegradable [4]. However, little research on its thermal transport properties has been conducted up to now. So few reporting on thermal conductivity and diffusivity is not due to a lack of interest, but to the difficulty of this kind of measurements in so extremely thin silk fibers (few micrometers in diameter). Furthermore, a surprising result has been recently published showing exceptionally high thermal diffusivity for spider dragline silk [5], about $70 \text{ mm}^2 \text{ s}^{-1}$, similar to the best thermal conducting metals. Motivated by this work, we have measured the thermal diffusivity of spider dragline silk by means of a method, based on lock-in thermography, that is specially designed to measure thermal diffusivity of very thin filaments [6,7]. This method was calibrated with filaments of thicknesses ranging from 5 to $150 \mu\text{m}$ in a wide range of diffusivities, from thermal insulators ($0.1 \text{ mm}^2 \text{ s}^{-1}$) to good thermal conductors ($300 \text{ mm}^2 \text{ s}^{-1}$) [7]. Results show a thermal diffusivity for the spider dragline silk about 400 times lower than the result found in Ref. [5] and falls within the typical diffusivity range of biomaterials ($0.1\text{--}0.3 \text{ mm}^2 \text{ s}^{-1}$).

2. Basics of the technique

The technique used for these measurements is Lock-in Infrared Thermography [8,9], which has been widely used to measure the thermal diffusivity of solid samples. It consists of illuminating the sample by a focused laser beam, modulated at a given frequency (f), while an infrared (IR) video camera records the surface temperature of the sample. A lock-in analysis of the image sequence at the modulation frequency provides the amplitude (T) and phase (Ψ) of the surface temperature. For thin filaments, heat propagation is one-dimensional from the heating spot along the filament. If the sample is kept in vacuum, only heat losses by radiation remain. Under this condition, linear relations are found when plotting the natural logarithm of the amplitude of the temperature ($\ln(T)$) and its phase (Ψ) as a function of the distance to the heating spot. The product of the slopes of these linear relations, $m_{\ln(T)}$ and m_{Ψ} , satisfies the following expression [6]

$$m_{\ln(T)} \times m_{\Psi} = \frac{\pi f}{D}, \quad (1)$$

from which the thermal diffusivity (D) of the filament can be obtained in a simple but accurate way [10].

3. Experimental results and discussion

The experimental setup is shown in Fig. 1. A continuous wave laser, whose intensity is modulated by an acousto-optic modulator, is focused onto the spider silk filament. The laser power is limited to a few tens of mW to prevent the silk from being damaged. An IR video camera (FLIR, model SC7500) records the temperature behavior along the filament. A microscope lens has been used to improve the spatial resolution, in such a way that each pixel

* Corresponding author. Tel.: +34 946014253.

E-mail address: agustin.salazar@ehu.es (A. Salazar).

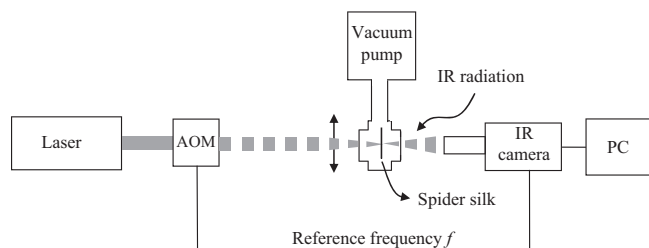


Fig. 1. Diagram of the experimental setup. The intensity of the laser is modulated by an acousto-optic modulator (AOM) and focused onto the spider silk filament. Then, IR radiation is emitted from the sample and detected by the IR camera, which processes the signal at the frequency reference (f) and sends the information to the PC for further analysis.

measures the average temperature over a square of $30\ \mu\text{m}$ in side. Low laser power together with low IR emissivity of the spider silk (data were collected on bare samples, i.e., without any coating) produce a temperature rise of the silk at the heating spot of a few tenths of K. In order to increase the signal to noise ratio a large number of images have been analyzed, since in Lock-in measurements the noise level is given by the following relation [9]

$$\text{Noise} = \frac{2}{\sqrt{N_{\text{images}}}} \text{NETD}, \quad (2)$$

where NETD is the Noise Equivalent Temperature Difference of the detector (20 mK in our camera) and N_{images} is the total number of images collected for the analysis. According to Eq. (2), by processing 10^6 images the noise level of the data was kept below 0.1 mK. As our camera works at a maximum rate of 350 images/s, collecting 10^6 images requires measurements as long as one hour. On the other hand, the samples have been placed inside a vacuum chamber (10^{-5} mbar) provided with sapphire windows, which are transparent to IR radiation. In this way, heat losses by convection and conduction to the surroundings are suppressed. Accordingly, only heat losses by radiation remain, so Eq. (1) can be applied. Each spider dragline silk filament, about 3 cm long, was trapped by the extremes in a sample holder. Careful rotation of the sample holder allows the filament to be aligned along an individual pixel column of the IR detector. The spider species we have studied is *araneus diadematus*, the so-called European garden spider, that is a common orb-weaver spider found throughout Europe and parts of North America. The diameter of its dragline silk filaments is around $5\ \mu\text{m}$.

Fig. 2 shows ψ and $\text{Ln}(T)$ of the spider dragline silk temperature as a function of the distance to the heating spot at $f=0.914$ Hz. As can be observed, good symmetry between left and right branches together with long straight lines covering several radians prove the quality of the data. In order to avoid damaging the fiber the temperature rise at the heating spot is only 0.15 K ($\text{Ln}(T) = -1.90$), while the noise level is below 0.1 mK ($\text{Ln}(T) < -9$). Continuous lines correspond to linear fittings. By applying Eq. (1) a thermal diffusivity value of $0.20\ \text{mm}^2\ \text{s}^{-1}$ is obtained. Note that the length of the silk filament used for the fitting is shorter than 4 mm, far away from the clamping points, thus avoiding any eventual influence from the sample holder. Besides, data were collected on different samples of dragline silk, and various modulation frequencies, ranging from 0.1 to 9 Hz, were tested in each specimen. From the statistical analysis, the resulting thermal diffusivity is $0.20 \pm 0.01\ \text{mm}^2\ \text{s}^{-1}$, which is about 400 times lower than the value reported in Ref. [5].

It is worth noting that not only was the dragline silk thermal diffusivity overestimated in Ref. [5], but also the value for the human head hair. Actually, the diffusivity obtained in Ref. [5] (0.42 – $0.47\ \text{mm}^2\ \text{s}^{-1}$) is 3 times larger than the true value [7] ($0.14\ \text{mm}^2\ \text{s}^{-1}$) corresponding to KERATIN, the material that hair, horns and nails are

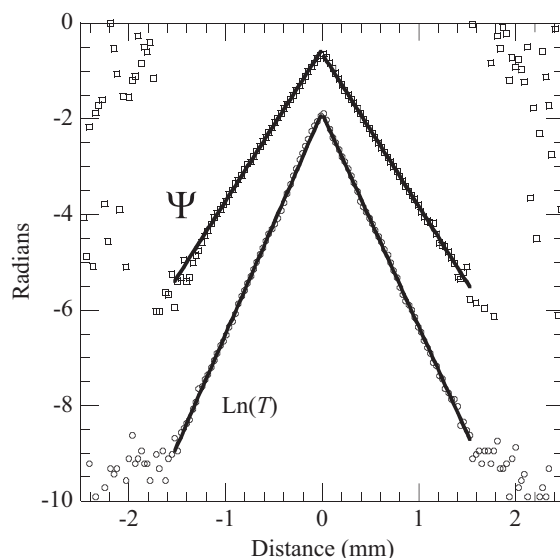


Fig. 2. Phase (ψ) and natural logarithm of the amplitude ($\text{Ln}(T)$) of a spider dragline silk temperature as a function of the distance to the heating spot, at $f=0.914$ Hz. Symbols correspond to experimental data and continuous lines to the linear fittings.

made of [11]. These anomalously high thermal diffusivity values of spider silk and human hair are likely related to methodological deficiencies. In fact, heat losses by radiation, which are noteworthy for micro-filaments, were not taken into account in the model [5,12]. As a consequence, the overestimation of the reported values on spider silk is much larger than on human hair because the diameter of the former is smaller ($4\ \mu\text{m}$ of spider silk versus $65\ \mu\text{m}$ of hair), and thus the effect of omitted heat losses, much more significant.

Certainly, we have not measured the thermal diffusivity of the silk of the same spider as in Ref. [5] *Nephila clavipes*, since it does not live in our country. However, such a huge difference in thermal diffusivity among different spider species is unlikely to happen. In fact, biomaterials have evolved over millions of years to improve physical properties for the benefit of living beings. That is the reason why the spider silk presents outstanding mechanical properties (high tensile strength, elasticity, toughness and ductility) but it remains thermal insulator.

4. Conclusion

Summarizing, measuring the thermal diffusivity of very thin fibers is a challenge. Using an appropriate experimental technique specially tailored to measure the thermal diffusivity of very thin filaments, the thermal diffusivity of the spider dragline silk has been obtained: $0.20 \pm 0.01\ \text{mm}^2\ \text{s}^{-1}$. Thus, the exceptionally high thermal diffusivity value of spider silk recently reported cannot be confirmed.

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