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2017-04-05

# Thermal Characterization of Natural and Synthetic Spider Silks by Both the $3\omega$ and Transient Electrothermal Methods

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## Original Publication Citation

Xing, C., Munro, T., Jensen, C., Ban, H., Copeland, C., and Lewis, R., "Thermal Characterization of Natural and Synthetic Spider Silks by Both the  $3\omega$  and Transient Electrothermal Methods," *Materials & Design*, 119, 2017.

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Munro, Troy; Xing, Changhu; Ban, Heng; Copeland, Cameron G.; Lewis, Randolph V.; and Jensen, Colby, "Thermal Characterization of Natural and Synthetic Spider Silks by Both the  $3\omega$  and Transient Electrothermal Methods" (2017). *All Faculty Publications*. 1875.  
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Troy Munro, Changhu Xing, Heng Ban, Cameron G. Copeland, Randolph V. Lewis, and Colby Jensen

1  
2 **Thermal Characterization of Natural and Synthetic Spider Silks by Both the  $3\omega$  and Transient**  
3 **Electrothermal Methods**

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9  
10 **Abstract**

11 Thermal conductivity, thermal diffusivity and volumetric heat capacity of three spider silks are measured in this  
12 paper as a benchmark for further studies. These silks include the major and minor ampullate silks of the *Nephila*  
13 *clavipes* spider, and a synthetic spider silk fiber made from recombinant dragline silk proteins purified from  
14 transgenic goats' milk. Two complementary measurement techniques are employed in the thermal characterization  
15 of these microscale single fibers for self-verification. One is the transient electrothermal technique (TET) and the  
16 other is the  $3\omega$  method. Experimental measurements indicate that thermal properties of the dragline silk are very  
17 close to those of the minor ampullate silk, whereas the ones for the synthetic silk are much lower due in part to its  
18 low crystallinity. The directly measured thermal conductivity, thermal diffusivity, and volumetric heat capacity of  
19 the major and minor ampullate silks are  $1.2\text{-}1.26 \text{ Wm}^{-1}\text{K}^{-1}$ ,  $5.7\text{-}6 \times 10^{-7} \text{ m}^2\text{s}^{-1}$ , and  $2\text{-}2.17 \text{ MJm}^{-3}\text{K}^{-1}$ , respectively. The  
20 thermal conductivity and thermal diffusivity of the as-spun synthetic silk are  $0.24 \text{ Wm}^{-1}\text{K}^{-1}$  and  $1.6 \times 10^{-7} \text{ m}^2\text{s}^{-1}$   
21 respectively. As part of this study, a detailed comparison of the TET and  $3\omega$  methods is provided showing the  
22 complementary nature of the techniques and illustrating the strengths and weaknesses of each.

23 Key words: 3-omega, spider silk, thermal characterization, transient electrothermal technique, synthetic silk

24  
25 **1. Introduction**

26 Naturally spun spider silk has many potential applications such as bullet proof vests, wear-resistance light clothing,  
27 ropes or parachutes, or artificial tendons or ligaments due to its favorable mechanical properties [1]. However, it  
28 cannot be produced in commercial scale quantities, which has led to the current development of synthetic (artificial)  
29 silk fibers by different approaches. The method used in the current study involves transferring silk producing genes  
30 to goats, causing the proteins to be expressed in the goats' milk, whereupon the proteins are purified into powders,  
31 and are then spun into large quantities of silk fibers with a modified plastic extruder [2]. Although variations in the  
32 spinning process (i.e. solvent baths and stretching) give rise to varying mechanical properties, this study focuses on  
33 the most basic "as-spun" fiber that experiences no additional processing after the fiber coagulation in isopropanol.

34 While mechanical properties of the spider silks have been measured with consistent results, thermophysical property  
35 measurements are still in the initial stage. Since silk is often touted as a replacement for petroleum-based aramids  
36 (such as Kevlar or Nomex), there is a need to also characterize its thermal properties for applications like thermal  
37 protective clothing, where aramid fibers are extensively used. For the natural spider silk, there are only two recent  
38 reports in the literature with reasonable thermal property values. Using a lock-in infrared thermography technique  
39 [3], the thermal diffusivity ( $\alpha$  [ $\text{m}^2\text{s}^{-1}$ ]) of the *Araneus diadematus* dragline silk was reported as  $2 \times 10^{-7} \text{ m}^2\text{s}^{-1}$ . From  
40 the transient electrothermal technique (TET) [4], thermal conductivity ( $k$  [ $\text{Wm}^{-1}\text{K}^{-1}$ ]) and thermal diffusivity of the  
41 *Nephila clavipes* dragline silk were determined as  $1.2 \text{ Wm}^{-1}\text{K}^{-1}$  and  $6 \times 10^{-7} \text{ m}^2\text{s}^{-1}$ , respectively. The measured thermal  
42 diffusivity by the authors [4] is within a factor of three to that in Ref. [3]. Therefore, confirmation of the result using  
43 another technique is necessary. Furthermore, thermal measurements of other types of silk, or of the synthetic silk  
44 fibers, have not been found in literature.

45 Two techniques (TET and  $3\omega$ ) have been investigated and successfully validated to determine the thermal  
46 conductivity and diffusivity (and the potential to directly measure the volumetric heat capacity,  $\rho C_p$  [ $\text{Jm}^{-3}\text{K}^{-1}$ ]) for  
47 single fibers by this group [5-8]. The former is based on the transient voltage response after the step input of a

1 constant direct current (dc), and the latter is analyzed from the steady-state, 3<sup>rd</sup> harmonic voltage amplitude and  
 2 phase responses based on a modulated alternating current (ac) heating. In this paper, thermal characterization of  
 3 individual fibers will adopt one or both of the techniques, depending on the fiber characteristics.

4 The objective of this paper is to determine the thermal properties of the natural and synthetic fibers. Because of the  
 5 differences in geometry and properties, a single method cannot measure all of the samples accurately. To this end,  
 6 technique selection for a specific fiber is provided by comparing the advantages and disadvantages of the two  
 7 methods based on sample geometry, property, and equipment availability. Thermal properties of the major ampullate,  
 8 minor ampullate, and synthetic silk fibers are then measured. This paper is crucial for the ongoing synthetic silk  
 9 production by providing a metric to direct synthetic production to more closely mimic natural spider silk properties.

10

## 11 2. Measurement techniques

12 Table 1 presents a comparative summary of the TET and  $3\omega$  measurement methods. Comparisons are made with  
 13 respect to measurement theory, procedure, data reduction, and accuracy.

14

### 15 A. Theoretical basis

16 In order to have a thermal measurement by either of the two methods, the sample needs to have a distinct (uniform)  
 17 geometry and a large aspect ratio ( $L/D > 10$ , where  $L$  is length [m] and  $D$  is diameter [m]). Additionally, it is  
 18 assumed that in the measured temperature range, the resistivity of the sample changes linearly with temperature, and  
 19 the temperature coefficient of resistivity ( $\alpha_T$  [ $K^{-1}$ ]) or of resistance ( $R'$  [ $\Omega K^{-1}$ ],  $R'=R_0\alpha_T$  where  $R_0$  [ $\Omega$ ] is the resistance  
 20 at temperature  $T_0$  [K]) needs to be known or calibrated. Samples are placed in a high vacuum chamber ( $<1 \times 10^{-3}$  -  
 21  $1 \times 10^{-4}$  Pa)[6] to reduce the lateral heat loss by convection. From the thermal response after heating, the  
 22 thermophysical properties are then obtained. Both methods use the same sample preparation methods and employ  
 23 Joule heating as a heat mechanism. The implementation of electrical heating and data detection steps are where the  
 24 techniques differ.

25

### 26 B. Heat transfer modeling

#### 27 B.1. TET

28 To perform the heating in TET, a constant dc current,  $I_d$  [A], is needed and can be provided by a precision current  
 29 source with a negligible settling time. When a constant dc current is applied, the conductive fiber or thin gold film  
 30 coating heats up. This temperature rise induces a change in resistance, which is monitored by a change in voltage as  
 31 a function of time. In this way, the sample's response evolves from its initial resistance,  $R_0$ , to the steady state value  
 32  $R_s$  [ $\Omega$ ], corresponding to an average temperature rise,  $\Delta T \rightarrow (0, \Delta T_s)$  [K]. Modeling of the heat transfer through the  
 33 sample has been given in a previous research [5], with the relevant equations for thermal property determination  
 34 summarized below.

$$35 \quad k = \frac{4I_d^2 R_0 R' L}{\pi D^2 (R_s - R_0)} \frac{2 - 2 \cosh(LH_e) + LH_e \sinh(LH_e)}{(LH_e)^3 \sinh(LH_e)} \quad (1)$$

$$36 \quad \frac{\Delta T}{\Delta T_s} = 1 - \frac{8(LH_e)^3 \sinh(LH_e)}{2 - 2 \cosh(LH_e) + LH_e \sinh(LH_e)} \times \sum_{n=1}^{\infty} \frac{e^{-[(2n-1)^2 \pi^2 + (LH_e)^2]at/L^2}}{[(2n-1)\pi]^4 + [LH_e(2n-1)\pi]^2}, \quad (2)$$

37 where  $H_e^2 = [(h_r + h_c)A_l - I_d^2 R'] / (kV_s)$  represents the heat loss from the radial surface and variable heating due to the  
 38 resistance change. The parameter  $h_r$  is the linearized radiation coefficient ( $h_r \approx 4\varepsilon\sigma T_0^3$ , where  $\varepsilon$  is emissivity and  $\sigma$  is  
 39 the Stefan-Boltzmann constant);  $h_c$  is the convective heat transfer coefficient [ $W m^{-2} K^{-1}$ ]; and  $A_l$  and  $V_s$  are the lateral

1 surface area [m<sup>2</sup>] and sample volume [m<sup>3</sup>], respectively. These additional terms are necessary for correct  
2 representation of the relevant heat transfer mechanisms and accurate property determination.

3 The temperature rise is usually limited to 2-10 K[4, 9], to minimize the heat generation drift ( $I_d^2 R'$ ) induced by the  
4 resistance change. However, for the coated, non-conductive samples, a low temperature rise causes relatively large  
5 error in the property measurements because of a low signal-to-noise ratio. Therefore, an optimal current is generally  
6 sought in the measurement to balance these two concerns. With negligible variation of heating and the high vacuum  
7 to minimize convection ( $h_c \approx 0$ ), the only term in  $H_e$  requiring special consideration is the radiation heat loss. This  
8 heat loss is independent of the temperature rise but not of the sample length. This will be discussed in the data  
9 reduction section.

10 To detect the transient response (Fig. 4 in Ref. [9]), a data acquisition unit/digital multimeter (DMM) with a fast  
11 sampling rate and high accuracy is needed. Depending on the sample length and thermal diffusivity, the sampling  
12 time varies from milliseconds to several hundred seconds.

13

### 14 B.2 $3\omega$

15 In the  $3\omega$  measurement, a modulated ac current, with an amplitude of  $I_0$  [A] and frequency of  $\omega$  [rad/s], is passed  
16 through the sample to generate electrical heating at the  $2\omega$  frequency. This induces a temperature response at  $2\omega$   
17 (negligible for higher harmonics), and then a  $2\omega$  response in the electrical resistance (Tab. 1). The voltage response  
18 then has harmonics at odd  $\omega$ . Detection of the voltage change is performed on the  $3\omega$  response ( $I_0 R' \cos \omega t \cdot \Delta T(2\omega t)$ )  
19 because it has the best accuracy. Modeling of the heat transfer by the  $3\omega$  method for thin fibers has been performed  
20 previously [7]. The detected voltage in a complex form is expressed by Eq. 3.

$$21 \quad V_3 = \frac{I_0^3 R_0' L}{k \pi D^2} \frac{2 - 2 \cosh(Lm) + Lm \sinh(Lm)}{L^3 m^3 \sinh(Lm)}, \quad (3)$$

22 where  $m^2 = i2\omega/\alpha + 4h_r/(Dk)$  represents the heating frequency and radiation influences on the measured voltage  
23 amplitude and phase responses. With negligible convective heat loss and nonconstant heating influences in both  
24 TET &  $3\omega$  measurements,  $m^2 = i2\omega/\alpha + H_e^2$ .

25 To experimentally detect the voltage response from Eq. 3, a lock-in amplifier is usually employed to monitor the 3<sup>rd</sup>  
26 harmonic frequency. With a continuous ac source heating the sample, the voltage amplitude and phase ( $\varphi$ ) are  
27 measured once they reach their steady state values. Usually, a frequency range that allows the phase to go between  
28 (0, -90°) is scanned to get the amplitude- or phase-frequency curve (Fig. 3 in Ref. [7]) used for the inverse problem  
29 of extracting thermal properties. Note that the voltage measured by a lock-in amplifier is a root-mean-square (rms)  
30 value.

31

### 32 C. Thermophysical property extraction process

33 Comparing Eq. 1 with Eq. 3 indicates that the radiation influence in the TET and  $3\omega$  technique ( $m$  or  $H_e$  terms) are  
34 the same, seen as  $4h_r/(Dk)$ . To account for radiation heat loss when  $\varepsilon$  is unknown, a model with dependency on one  
35 thermal property is used to calculate that property and  $\varepsilon$ . Then the other property is determined with the now  
36 calculated  $\varepsilon$  value.

37 For the TET, thermal conductivity and diffusivity are obtained from Eq. 1 and 2. However, since the radiation  
38 influence cannot be avoided, multiple length samples are necessary to separate the radiation contribution from the  
39 measured thermal properties. One approach ( $k, \varepsilon \rightarrow \alpha$ ) uses Eq. 1 to determine  $k$  and  $\varepsilon$ . Eq. 2 is then used to obtain  $\alpha$ .  
40 For samples with large uncertainty from measured  $R'$ , this procedure renders large error. For such samples, the  
41 suggested process ( $\alpha, H_e \rightarrow k$ ) is to start from Eq. 2 to determine  $\alpha$  and  $H_e$ . With  $H_e$ , the  $k$  of each sample can then be  
42 determined by Eq. 1. The latter procedure is preferred because of lower precision uncertainties in measured thermal  
43 diffusivity [9] than thermal conductivity.

44 For the  $3\omega$  method, thermal conductivity, diffusivity, and volumetric heat capacity (which is equal to the product of  
45 density  $\rho$  [kgm<sup>-3</sup>] and specific heat capacity  $C_p$  [Jkg<sup>-1</sup>K<sup>-1</sup>]) can be determined independently from Eq. 3 at different  
46 frequency ranges. At frequencies where  $\varphi < -5^\circ$  (i.e. low-frequency range), the amplitude from Eq. 3 becomes

1 independent of frequency and dependent only on thermal conductivity (and radiation heat loss). Similar to the TET,  
2  $k$  can be obtained by curve-fitting based on property measurements of samples at different lengths or by knowing  $H_e$ .

3 Within the frequency range where  $-90^\circ < \varphi < -89^\circ$  (i.e. high-frequency range), the amplitude from Eq. 3 depends on  
4 the product of  $\rho C_p$  only. Radiation has little effect on the amplitude response in this frequency range, which is an  
5 advantage of the direct measurement of  $\rho C_p$ . However, the signal becomes much weaker and susceptible to system  
6 noise. To measure an equivalent amplitude response similar to that seen at low frequencies, the temperature rise has  
7 to become large, which may violate the constant heating assumption. However, even with these uncertainties, the  
8 direct determination of  $\rho C_p$  is still one of the benefits of the  $3\omega$  measurement.

9 In the middle frequency range, the phase-frequency response is used for thermal diffusivity evaluation by direct  
10 fitting of Eq. 3. The regression is similar to the second procedure for TET ( $\alpha, H_e \rightarrow k$ ) but is easier because fewer data  
11 points are typically measured in the  $3\omega$  method.

#### 13 D. Selection considerations for both techniques

14 *Properties Determined:* The  $3\omega$  technique allows three properties ( $k, \alpha, \rho C_p$ ) to be measured simultaneously and  
15 independently. This prevents the propagation of uncertainty from two parameters when calculating the third ( $\rho C_p = k/\alpha$ ).  
16 From the TET, however, only  $k$  and  $\alpha$  are available for simultaneous determination.

17 *Accuracy:* The  $3\omega$  technique has better accuracy than the TET. The amplitude of  $3\omega$  measurements is a function of  
18 only sample resistance,  $R_0$ , whereas for the TET, thermal conductivity is derived from the temperature rise resulting  
19 in the change of sample resistance,  $R_s - R_0$ . The resistance change in the measurement is only several thousandths or  
20 ten-thousandths of the sample resistance, producing larger precision uncertainties in the TET. Uncertainties  
21 associated with the correct selection of the initial unheated resistance from the transient curve and good acquisition  
22 of the transient nature of the heating effect [9] further decrease the accuracy of the TET approach. The  $3\omega$  measures  
23 the signal in a steady-state manner, which improves the accuracy of the phase and amplitude by averaging the signal  
24 over a period of time.

25 *Measurement Time:* The advantage of the TET over the  $3\omega$  method is in measurement time, from milliseconds to  
26 hundreds of seconds depending on the sample length and diffusivity. In comparison, the  $3\omega$  method typically require  
27 minutes to hours to reach steady-state conditions at a single frequency. For high diffusivity samples,  $3\omega$  is the  
28 preferred choice due to the better accuracy. For low diffusivity samples, if the diameter is sufficiently small such  
29 that the radiation influence is significant (e.g. natural spider silks), the  $3\omega$  technique is favorable. But if the diameter  
30 is large and the samples are long (e.g. synthetic spider silk), the TET has advantages due to the prohibitively long  
31 measurement time of the  $3\omega$  method (at frequencies  $< 0.01$  Hz).

32 *Radiation Influence:* Both methods suffer from the radiation heat loss influence, therefore, it is infeasible to get the  
33 precise property measurement with one sample. Tests at various lengths need to be performed before to ensure  
34 proper accounting of radiation heat transfer effects.

### 36 3. Samples and tests

#### 37 A. Silks

38 Thermal properties of dragline (major) silk of the *Nephila clavipes* have yet to be measured and verified by the  $3\omega$   
39 method, but have been investigated using the TET in a previous research [4]. This major ampullate silk is comprised  
40 of two proteins, MaSp1 and MaSp2. In this paper, data reduction on the TET measurements will be conducted based  
41 on direct diffusivity measurements ( $\alpha, H_e \rightarrow k$  in Sec. 2C), and compared with results from the direct measurements  
42 of the conductivity ( $k, \varepsilon \rightarrow \alpha$ ) [4]. In the  $3\omega$  measurement, one fiber was broken from set (a sample set is defined in  
43 Sec. 3B) #2, thus leaving 12 samples of the original 13 from Ref [4]. However, the broken fiber was not replaced  
44 because there would have been a need for additional coating and annealing, but the broken fiber did not cause any  
45 problems to the silk measurements. The diameter of the major silk was  $3.1 \pm 0.2 \mu\text{m}$ , measured by a scanning electron  
46 microscope (SEM). The silks on each sample mount set are taken from the same strand of spider silk.

47 Minor ampullate silk is produced from the minor ampullate gland of the spider and is comprised of MiSp1 and  
48 MiSp2 proteins. These proteins have similar secondary structures to the major ampullate or dragline silk, but not all

1 structures are present, nor are all mechanical properties the same. The primary structures of the two silks are  
2 distinctly different [10], and the extensibility and tensile strength are different. Additionally, minor ampullate  
3 contains complex spacers that are not in major ampullate silk [11], while major ampullate silk has GPGXX motifs  
4 which are responsible for the extensibility of the silk. The diameter of the minor ampullate silk was  $2\pm 0.2\ \mu\text{m}$  under  
5 SEM measurement. Three sets of samples have been prepared and measured by both techniques for comparison.

6 Both major and minor ampullate silk was collected from adult *N. clavipes* spiders, which originated from Florida,  
7 US, using the method described by Xu et al. [12] (similar to Ref. [13]). Briefly, spiders were restrained on the top of  
8 a Petri dish and anesthetized by exposing them to  $\text{CO}_2$ . The spider's spinnerets were located with a dissecting  
9 microscope and using tweezers, whereupon the silk was teased out of either the major or minor ampullate gland. The  
10 silk was attached to a rotating spool and was gathered continuously at a silking rate of about 2 m/min. During the  
11 spooling procedure, the spiders were misted with water. Samples placed on the heat sinks of each measurement set  
12 were unwound from these spools so that all samples on all the sets came from the same strand of silk.

13 The protocol for synthetic silk gene cloning, protein expression, protein purification, and fiber formation is detailed  
14 in Refs. [14-16], and a summary of the relevant processes is given. The dragline proteins, MaSp1 and MaSp2, were  
15 expressed in the milk of different goat herds. The protein was then extracted and purified from the milk, resulting in  
16 a white powder. For the current study, a ratio of 80% MaSp2 to 20% MaSp1 by weight for the proteins was  
17 dissolved in Hexafluoro-2-propanol (HFIP) to create a dope (about 20% weight/volume (w/v) concentration of  
18 protein in the dopes). The dope was then pushed out of a small diameter syringe ( $254\ \mu\text{m}$ ) into a 100% isopropanol  
19 bath, which caused the dope to coagulate. The coagulated, extruded silk was then fed through godets and collected  
20 on a winder. These "as spun-fibers" (no additional treatment, except for the coagulation bath) were selected for  
21 thermal property characterization because of their uniform geometry, in addition to providing a benchmark property.  
22 Under SEM, the diameter was  $51.7\pm 1\ \mu\text{m}$ . Because of its large diameter (less radiation influence) and low expected  
23 thermal conductivity, the synthetic fiber was mainly measured by TET. For the shortest synthetic fiber, which  
24 required a modulation frequency near 0.005 Hz to get thermal conductivity, the  $3\omega$  technique is used to verify the  
25 TET measurements.

26 SEM pictures of the three types of fibers are presented in Fig. 1.

## 27 B. Sample preparation and equipment

28 Preparation of the electrically non-conductive samples for both TET and  $3\omega$  has been detailed elsewhere [9]. Briefly,  
29 one end of a sample is mounted on a common heat sink and the other was separately secured on a different heat sink  
30 terminal. This process was repeated several times until silks from the same strand were placed on a sample mount  
31 set. Because the silks were from the same strand, there was little difference between the behavior of each set. The set  
32 of samples underwent gold sputter coating, annealing, and its temperature coefficient of resistivity was calibrated in  
33 an isothermal enclosure. The two measurement techniques were then employed with the samples placed in a high  
34 vacuum chamber. The number of samples on a mount is limited by the size of the gold sputter coater thus a  
35 maximum of 8 samples were prepared in a set. However, because of coating defects, not all samples exhibited a  
36 measurable resistance and could therefore be measured. Because the thermal property measurement of the dragline  
37 silk by TET [4] revealed lower thermal properties than originally expected, the minor ampullate silk sample sets  
38 were prepared with shorter sample lengths to reduce measurement times.

39 Water content in silk has the effect of increasing the storage modulus of the fiber when the water is removed [17],  
40 which results in a glassy rather than rubbery state of the silk [18]. With regard to the loss of water by the silk during  
41 the coating process and property measurement, the silk is expected to have a slightly higher property than if the  
42 fibers were in a state of supercontraction due to a high relative humidity. All other thermal property measurements  
43 of silk in the literature have also employed high vacuum.

44 For the TET measurement, a Keithley 6221 current source with a short settling time was selected for the constant dc  
45 heating. A Keithley 3706 DMM was employed to monitor the voltage change in a four wire resistance measurement  
46 configuration. For the  $3\omega$  measurement, an SR 850 lock-in amplifier was employed to both provide a constant ac  
47 voltage and monitor the 3<sup>rd</sup> harmonic voltage response (complex number). The sample was connected to a custom  
48 Wheatstone bridge, and conversion of the constant voltage output to constant current models can be found in Ref.  
49 [7]. In the  $3\omega$  measurement, a Keithley 6221 in ac mode was also employed for some samples as a comparison.

1 Thermal properties of the fibers were determined by the equations in Sec. 2B and methods in Sec. 2C.

2

### 3 4. Results and discussion

4 The thermophysical properties of the three silk samples (dragline, minor ampullate, and synthetic) are discussed in  
5 this section. Figures showing the variation with respect to length will be presented to demonstrate how the full  
6 model corrects for radiative heat losses to improve measurement accuracy.

#### 7 *Dragline Silk TET:*

8 Figure 2 presents the thermal diffusivity and thermal conductivity of the dragline silk measured by the TET ( $\alpha$   
9  $=5.9 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ ,  $k=1.18 \text{ Wm}^{-1} \text{ K}^{-1}$ ). Data reduction for property extraction employs the second approach in Sec. 2C  
10 ( $\alpha, H_e \rightarrow k$ ), namely getting  $\alpha$  and  $H_e$  from Eq. 2 by regression on 13 sample measurements. Then  $k$  can be obtained  
11 from Eq. 1 by the knowledge of  $H_e$ . A least-squares regression method is used to obtain  $k$  or  $\alpha$ . Because radiation  
12 heat loss significantly influences the measured thermal property, the measured thermal conductivity (neglecting heat  
13 loss) varies from 1.2 to  $\sim 200 \text{ Wm}^{-1} \text{ K}^{-1}$ , depending on the sample length (Tab. 1 in Ref. [4]). The determined thermal  
14 conductivity and diffusivity by the second approach ( $\alpha, H_e \rightarrow k$ ) compared with those obtained using the first  
15 approach ( $k, \epsilon \rightarrow \alpha$  in Ref. [4]) show small differences. The comparison provides evidence of reliable measurement  
16 for both the thermal conductivity and diffusivity since it is not model dependent. Separate regressions using Eq. 1 or  
17 2 uncouple  $k$  and  $\alpha$ , and are thus not recommended in the characterization. Consistency of the results provide greater  
18 confidence that the results are independent of the data processing approach and related only to the thermal behavior  
19 of the samples.

#### 20 *Dragline Silk $3\omega$ :*

21 Figure 3 presents a dragline silk measurement by the  $3\omega$  technique. When  $\varphi > -5^\circ$ , the amplitude response stays  
22 almost constant and depends only on sample  $k$  and  $LH_e$  ( $H_e$  is the unknown and  $LH_e$  is dimensionless whereas  $m$  has  
23 frequency contribution). With the assumption that  $LH_e \rightarrow 0$ ,  $k$  can be determined directly, with the results presented  
24 in Tab. 2 as the R (reduced) column. Similar to Fig. 3,  $k$  of other silks at multiple lengths is also determined and  
25 presented in Tab. 2. As can be seen from the table, the calculated  $k$  varies in two orders of magnitude, which  
26 indicates a significant heat loss effect, and thus, the need for the full Eq. 3. With the least-squares minimization, a  
27 regressed  $k$  and  $H_e$  can be obtained and the individual  $k$  of each sample is presented in Tab. 2 as the F (full) column.

28 In the middle frequency range of Fig. 3, the phase response is used for the  $\alpha$  determination of the dragline silk.  
29 Using the previously calculated  $H_e$ , the determined  $\alpha$  with and without included heat loss effects is presented in Tab.  
30 2. As observed in the earlier  $k$  determination, significant heat loss contribution is found as the length of the fiber  
31 increases. At the high frequency range (which also corresponds to when  $\varphi \rightarrow -90^\circ$ ), the amplitude is employed to  
32 determine  $\rho C_p$ . The directly measured  $\rho C_p$  given in the table is comparable to the value calculated by  $k/\alpha$ .

33 Figure 4 summarizes the measured  $k$ ,  $\alpha$ , and  $\rho C_p$  of dragline silk in Tab. 2 and further presents the properties  
34 determined from the approach of  $\alpha \rightarrow k$  (Fig. 4b). As can be seen from Fig. 4a and 4b, the results are almost identical.  
35 The directly measured  $\rho C_p$  (Fig. 4c) is used to verify the accuracy of the former two properties ( $k$  and  $\alpha$ ). As shown  
36 in the figure, the directly measured  $\rho C_p$  is only 2% different from that computed from  $k/\alpha$ . In addition,  
37 measurements by the  $3\omega$  technique confirm the results presented in Ref. [4]. The scatterings (two standard  
38 deviations about the mean of the measurements) are respectively 15%, 12%, and 15% for  $\alpha$ ,  $k$ , and  $\rho C_p$   
39 measurements.

#### 40 *Minor Ampullate Silk TET and $3\omega$ :*

41 The minor ampullate silk has been measured by the two techniques, and the results are presented in Fig. 5 and Tab.  
42 3. For both, the thermal diffusivity is determined, with  $H_e$  determination being the first step in the data processing ( $\alpha$ ,  
43  $H_e \rightarrow k$ ). As shown in Fig. 5b, several outliers are neglected from the  $k$  and  $\rho C_p$  dataset based on Chauvenet's  
44 criterion. These outliers are likely ascribed to diameter uncertainty, the calibration of  $R'$ , or coating defects for that  
45 particular sample. Calibration of  $R'$  was conducted several times but none of the calibrations yielded a reasonable  $k$   
46 value. However, these defects do not affect the accuracy of  $\alpha$ , because thermal diffusivity determination employs a  
47 dimensionless transient curve for TET and non-dimensional phase response for  $3\omega$ . In the data reduction process, all  
48 of the samples are incorporated in the  $\alpha$ -regression process and, by using the full models, length considerations were  
49 taken into account. Measured properties of minor ampullate silk ( $\alpha = 5.7 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ ,  $k = 1.26 \text{ Wm}^{-1} \text{ K}^{-1}$ , and  $\rho C_p = 2.17$



1 MJm<sup>-3</sup>K<sup>-1</sup>) are close to those of the major silk, with measurement scatterings of 12%, 19%, and 20% for  $\alpha$ ,  $k$ , and  
2  $\rho C_p$ , respectively. These values do not vary significantly from the major ampullate silk, although their mechanical  
3 properties such as extensibility and tensile strength do. The explanation for this is the independence of thermal  
4 conductivity on those properties, but by way of a well-known kinetics model for the thermal conductivity of a  
5 material ( $k=1/3 \rho C_p v \lambda=C_p \lambda (E\rho)^{-0.5}$ , where  $v$  is the speed of the heat carrier [ms<sup>-1</sup>] – which are phonons in the case of  
6 silk,  $\lambda$  is the mean free path of the heat carrier [m], and  $E$  is the Young's Modulus [GPa]), the key properties for  
7 thermal conductivity,  $k$ , are specific heat and Young's modulus. The work of Koski [19] has shown that the elastic  
8 moduli of major and minor ampullate silks from the *N. clavipes* spider is not significantly different. Since these  
9 values do not contribute to ultimate tensile strength of extensibility of the silk, having similar thermal properties but  
10 different mechanical properties is reasonable.

#### 11 *Synthetic Silk TET and 3 $\omega$ :*

12 The synthetic silk's thermal properties are presented in Fig. 6 and Table 4. This fiber is mainly measured by the TET,  
13 because the  $H_e$  term is much smaller due to its relatively large diameter. To verify the TET measurements, the 3 $\omega$   
14 technique is also used for the shortest sample. Diffusivity and conductivity of the synthetic fiber are 1.6x10<sup>-7</sup> m<sup>2</sup>s<sup>-1</sup>  
15 and 0.24 Wm<sup>-1</sup>K<sup>-1</sup>, respectively. Using the measured thermal conductivity and diffusivity, the volumetric heat  
16 capacity may be calculated as 1.5 MJm<sup>-3</sup>K<sup>-1</sup>, ~25% lower than the natural spider silk. For the synthetic fiber  
17 measurements, the scatterings are 15% and 13% for  $\alpha$  and  $k$  measurements, respectively.

18 Thermal conductivity and diffusivity of the synthetic fiber is much smaller than the natural silk, which agrees with  
19 its low degree of crystallinity and lower mechanical properties (particularly Young's Modulus) compared to the  
20 dragline silk [20, 21]. For conditions that require thermal insulation, the synthetic fiber is more suitable; for  
21 conditions that necessitate larger thermal conductivity, other treatments on the as-spun fiber (that increase the  
22 crystallinity and mechanical properties of the fiber [2]) may be able to improve the thermal properties. This  
23 improvement comes from the formation and axial alignment of crystalline  $\beta$ -sheets that are expected to have a  
24 higher thermal conductivity than the amorphous regions of the fiber [22]. Such treatments are under investigation  
25 but currently produce a fiber with a non-uniform geometry [23, 24], which creates large uncertainty on the measured  
26 property values.

27 It should be noted that the influence of the metallic coating on the measured thermal properties has been investigated  
28 previously [9], but the change of measured property values due to an increase of coating thickness (10 nm to 20 nm)  
29 is within the uncertainty range of measurements ( $\pm 5\%$ ) [9]. The relative roughness of the synthetic silk is not  
30 expected to double the coating thickness size, nor affect the property measurement within the current uncertainty  
31 bounds. The uncertainty caused by the coating is primarily related to nonuniformity in the coating and the fact that  
32 the metallic film (10nm) behaves differently (non-constant resistivity and significant thermal conductivity drop)  
33 from the bulk material, even after annealing [4, 9].

34

## 35 **5. Conclusions**

36 To aid in the selection of an appropriate technique for the thermophysical property measurements of different spider  
37 silks (or thin fibers), the advantages and disadvantages of the TET and steady-state 3 $\omega$  method are compared with  
38 respect to measurement theory, data processing, and measurement accuracy. The 3 $\omega$  technique generally has a better  
39 measurement precision and is preferred, if feasible. For samples that would experience a prohibitively long  
40 measurement time with the 3 $\omega$  method, the TET is a reliable alternative.

41 Data processing where the thermal diffusivity and radiation influence is determined first and the conductivity  
42 determination is done based on those results ( $\alpha$ ,  $H_e \rightarrow k$ ) is preferred because only dimensionless data are required.  
43 Coating anomalies or other defects that significantly affect the thermal conductivity or heat capacity measurements  
44 have little influence on the accuracy of thermal diffusivity evaluation relative to other measurement uncertainties.

45 Experimental measurements indicate that the minor ampullate silk has equivalent thermal properties to the major  
46 silk. The thermal conductivity and diffusivity of the untreated, as-spun synthetic silk fiber are respectively ~1/5 and  
47 ~1/4 of the properties of the natural dragline spider silk, primarily attributed to its low degree of crystallinity. The  
48 results also demonstrate the use of these techniques as a powerful tool for providing comparative metrics directly  
49 linked to material microstructure. Such metrics will aid development of synthetic production of spider silk to more  
50 closely mimic natural spider silk properties.

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## Acknowledgments

Partial support by Utah Science Technology and Research (USTAR) initiative funding. The gold coating and SEM work were performed by FenAnn Shen at the Nanoscale Device Laboratory, USU.

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6 *Flagelliform Silk-Like GGX Motifs Contribute to Extensibility and Spacer Motifs Contribute to Strength in*  
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Table 1 Comparison between the TET and  $3\omega$  method

	$3\omega$	TET
Requirement for method applicability	Known or calibrated constant temperature coefficient of resistivity ( $\alpha_T$ ) such that $R(T)=R_0(T_0)[1+\alpha_T(T-T_0)]$	Same
Sample preparation	Suspended conductive wire or metal-coated non-conductive fiber on heat sinks with well-defined geometry ( $L, D$ )	Same
Testing conditions	High vacuum ( $< \sim 0.001\text{Pa}$ ) to minimize convective heat transfer	Same
Measurement theory	Modulated Joule heating	Transient Joule heating
Heating type	ac current modulated at $1\omega$	Constant dc current
Heating magnitude ( $\Delta T$ )	$\sim 1/5$ of the required heating magnitude by TET	Higher to improve signal strength (unfortunately also induces larger temperature rise, 2-10K)
Detection type	Steady-state voltage amplitude and phase at $3\omega$ of heating frequency via lock-in amplifier	Fast DMM detection during transient temperature increase to reach steady-state
Detection accuracy	High for the fundamental harmonic signal is cancelled	Less, because of the uncertainty in Joule heating initiation, and negligible resistance change compared to the bulk sample resistance (signal-to-noise-ratio)
Thermal conductivity ( $k$ )	From low frequency voltage amplitude, proportional to sample resistance, high accuracy	From steady-state temperature rise, proportional to sample resistance change by temperature rise, medium accuracy
Volumetric heat capacity ( $\rho C_p$ )	From high frequency voltage amplitude, susceptible to noise, medium accuracy	Unable to determine directly
Thermal diffusivity ( $\alpha$ )	Regression based on phase at different frequencies, high accuracy	Regression on the transient temperature rise curve, medium to high accuracy
Radiation influence ( $h_r$ )	Same influence but the correction is easier to perform based on thermal conductivity (amplitude) or thermal diffusivity (phase)	Length independency needs to be checked for the same samples with same treatments. Correction is necessary at significant levels of influence.
Variable heating influence ( $I_a^2 R'$ or $I_0^2 R'$ )	Not necessary because of less heating	Necessary, if larger temperature rise is required for better precision
Measurement length of time	Long (minutes)	Quick (seconds)
Equipment	Lock-in amplifier and either modulated current supply or bridge circuit for voltage supply	DMM and constant current supply

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1 Table 2 Measurement of *dragline silk* by the  $3\omega$  technique. Fiber diameter  $D$ :  $3.1\mu\text{m}$ ;  $V_3$ : rms voltage measured by  
 2 lock-in amplifier when  $\varphi > -5^\circ$ . It was observed that resistances have a slight change after TET measurements. (R:  
 3 reduced model of Eq. 3 which neglects heat loss ( $h_r=0$ ) and F: full Eq. 3)

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Set #	$L$ (mm)	$R_0$ ( $\Omega$ )	$R'$ ( $\Omega\text{K}^{-1}$ )	$I_0$ ( $\mu\text{A}$ )	$V_3$ ( $\mu\text{V}$ )	$k$ ( $\text{Wm}^{-1}\text{K}^{-1}$ )		$\alpha$ ( $\text{mm}^2\text{s}^{-1}$ )		$\rho C_p$ ( $\text{MJm}^{-3}\text{K}^{-1}$ )
						R	F	R	F	
1	3.84	6134.5	5.82	5.5	4.61	9.65	1.35	4.09	0.54	2.29
2	4.53	4914.2	4.76	7.41	7.52	11.18	1.18	5.83	0.57	2.05
2	7.86	7469.1	7	6.81	8.16	31.07	1.21	16.91	0.59	1.96
2	12.31	15306.7	11.24	5.08	7.42	72.86	1.22	42.96	0.62	1.9
3	0.32	792.2	0.63	25	3.95	1.24	1.19	0.58	0.56	2.14
3	1.47	2221.8	2.19	8.5	3.86	2.23	1.15	1.22	0.62	2.02
3	8.83	8939.9	10.33	4.5	3.56	40.74	1.28	21.21	0.59	1.99
3	13.97	16307.4	18	3.5	3.53	97.21	1.27	51.94	0.58	1.86
3	20.24	31436.5	32.08	3.13	6.54	186.36	1.19	118.13	0.64	1.87
4	1.08	1827.1	1.86	13	7.62	2.06	1.37	1.04	0.68	1.95
4	6.46	12435	10.62	4	4.54	23.45	1.31	12.19	0.62	2.26
4	11.62	37611.5	27.05	2.5	5.57	64.68	1.2	41.27	0.67	1.79
Mean							1.24		0.61	

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Table 3 Measurement of minor ampullate silk by the  $3\omega$  technique. Fiber diameter  $D$ : 2  $\mu\text{m}$ ;  $V_3$ : rms voltage measured by lock-in amplifier when  $\phi > -5^\circ$ . (R: reduced model of Eq. 3 which neglects heat loss ( $h_r=0$ ) and F: full Eq. 3). Outliers (grey color) are included in the reduced model &  $\rho C_p$  measurement, which demonstrates the merit of regression based on thermal diffusivity.

Set #	$L$ (mm)	$R_0$ ( $\Omega$ )	$R'$ ( $\Omega\text{K}^{-1}$ )	rms $I_0$ ( $\mu\text{A}$ )	$V_3$ ( $\mu\text{V}$ )	$k$ ( $\text{Wm}^{-1}\text{K}^{-1}$ )		$\alpha$ ( $\text{mm}^2\text{s}^{-1}$ )		$\rho C_p$ ( $\text{MJm}^{-3}\text{K}^{-1}$ )
						R	F	R	F	
1	0.59	726	0.56	21.8	8.4	3.87		0.75	0.59	5.64
1	1.26	2965	1.9	5.77	7.09	2.55	1.18	1.3	0.59	2.11
1	2.46	4220	2.67	5.76	7.94	8.83		2.92	0.52	3.25
1	3.7	5152	5.17	4.28	6.72	15.2	1.44	6.89	0.6	2.46
1	5.14	9520	8.34	3.34	7.9	25.5	1.33	11.8	0.55	2.45
2	0.44	1653	1.25	16.4	7.89	6.81		0.69	0.6	10.7
2	0.91	2523	1.78	8.29	8.31	3.73		0.85	0.52	4.86
2	2.97	4512	4.1	4.97	9.7	9.24	1.27	4.75	0.61	2.03
2	4.23	9824	8.69	3.1	7.8	18.2	1.36	8.71	0.59	2.32
3	0.34	1530	0.93	14.6	9.28	2.16		0.59	0.54	4.01
3	3.48	4755	4.97	4.29	7.24	11.87	1.25	6.14	0.6	2.14
3	7.41	9116	9.14	3.32	7.2	41.6	1.1	23.3	0.54	1.96
3	8.4	21480	18.64	2.16	8.27	54	1.13	29.9	0.54	1.91
Mean							1.26		0.57	2.17

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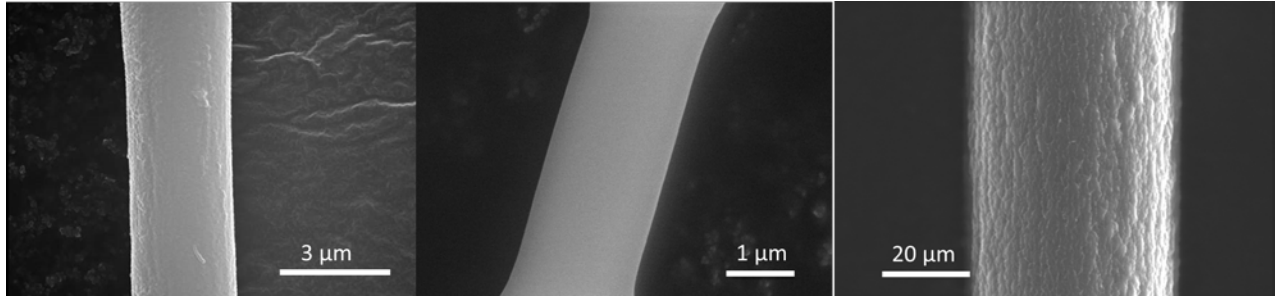
1 Table 4 Measurement of *synthetic silk* by the TET (R: reduced model of Eq. 3 which neglects heat loss ( $h_r=0$ ) and F:  
 2 full Eq. 3). Fiber diameter  $D$ : 51.7 $\mu$ m  
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Fiber #	$L$ (mm)	$R_0$ ( $\Omega$ )	$R'$ ( $\Omega K^{-1}$ )	$k$ ( $Wm^{-1}K^{-1}$ )		$\alpha$ ( $mm^2s^{-1}$ )		$\rho C_p$ ( $MJm^{-3}K^{-1}$ )
				R	F	R	F	
1	1.72	681.2	0.443	0.34	0.25	0.22	0.16	
1 (3 $\omega$ )	1.72			0.34		0.22		
2	3.69	1169.8	0.786	0.63	0.24	0.46	0.17	
3	6.12	1029.4	0.719	1.12	0.22	0.93	0.16	
4	8.83	1178.4	0.858	2.29	0.24	1.56	0.15	
5	11.02	1676.8	1.206	3.44	0.24	2.30	0.15	
6	12.12	2335.2	1.589	3.98	0.24	3.16	0.17	
7	13.83	5205.0	3.332	5.74	0.27	4.35	0.18	
Mean					0.25		0.16	1.5

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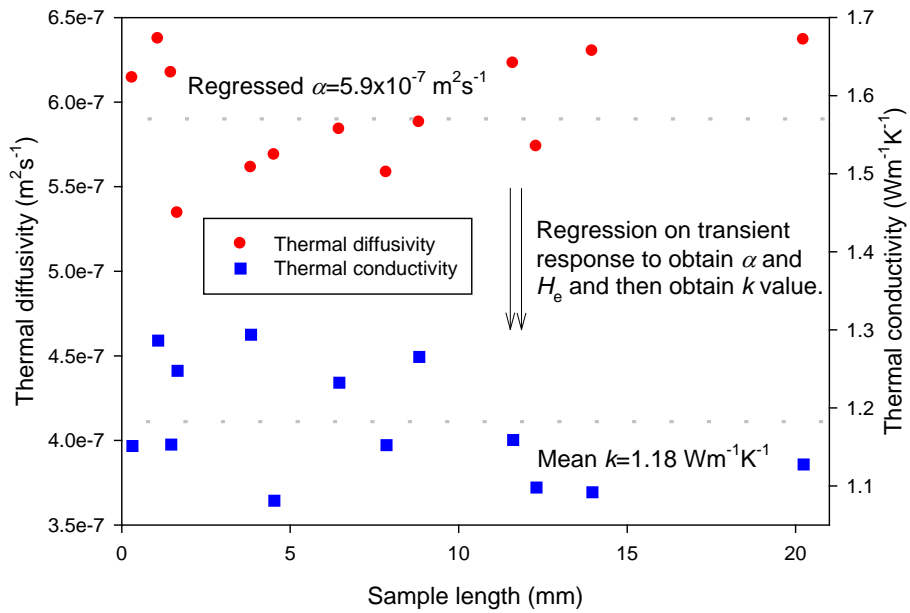
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Fig. 1 SEM images of natural dragline silk (left, 3 μm scale bar), minor ampullate silk (center, 1 μm scale bar), and as-spun synthetic silk (left, 20 μm scale bar).

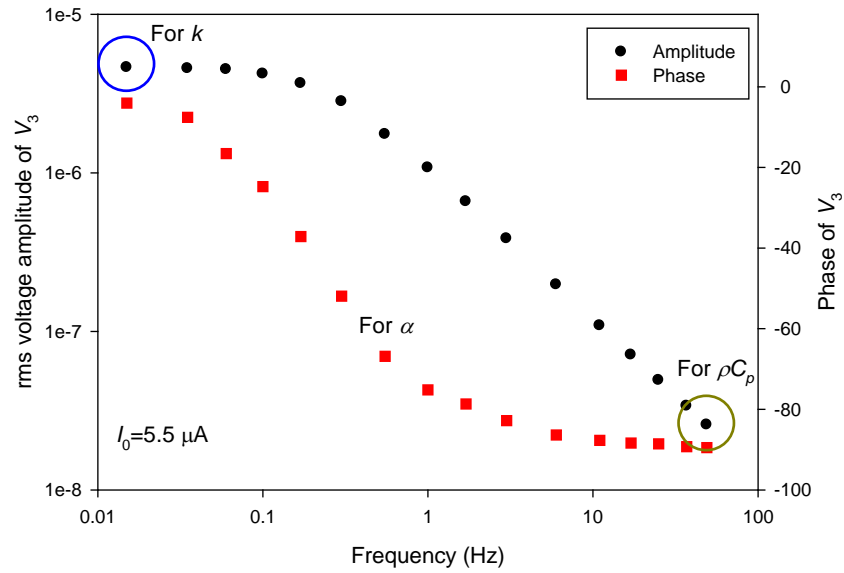


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Fig. 2 Thermal properties of dragline spider silk measured by the TET. Thermal diffusivity and radiation contribution were determined first and then thermal conductivity ( $\alpha, H_e \rightarrow k$ ) was obtained by incorporating the found radiation influence. Similar results are found using conductivity models first and then diffusivity models ( $k, \epsilon \rightarrow \alpha$ ).



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Fig. 3  $3\omega$  measurements of one *dragline silk* sample,  $L=3.84$  mm, demonstrating the measured amplitude and phase behavior as a function of frequency, as well as regions of the data used for determination of the different thermophysical properties.

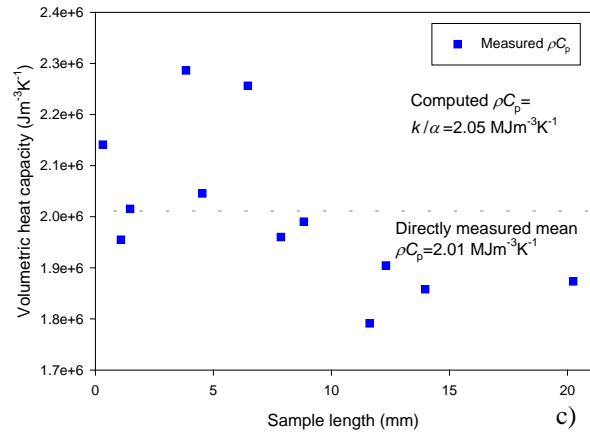
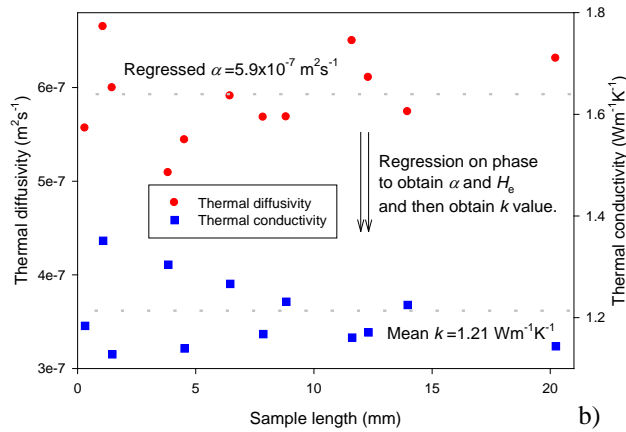
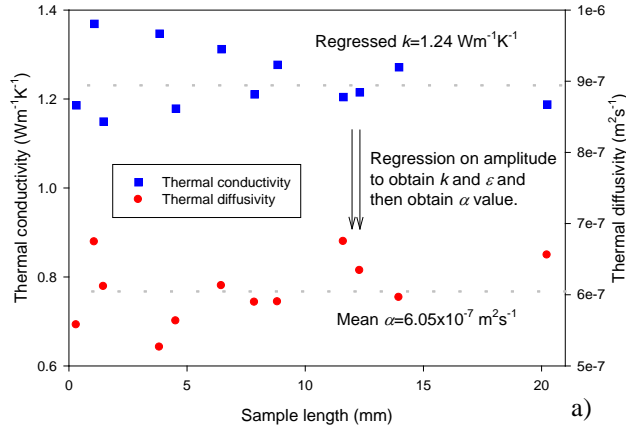


Fig. 4 Thermal conductivity, thermal diffusivity, and volumetric heat capacity of the *dragline silk* by the  $3\omega$  technique, a) regression on amplitude to get conductivity and emissivity and then obtain diffusivity, b) regression on phase to get diffusivity and radiation effect and then obtain conductivity, c) directly measured volumetric heat capacity versus computed from  $k/\alpha$ , showing good agreement.

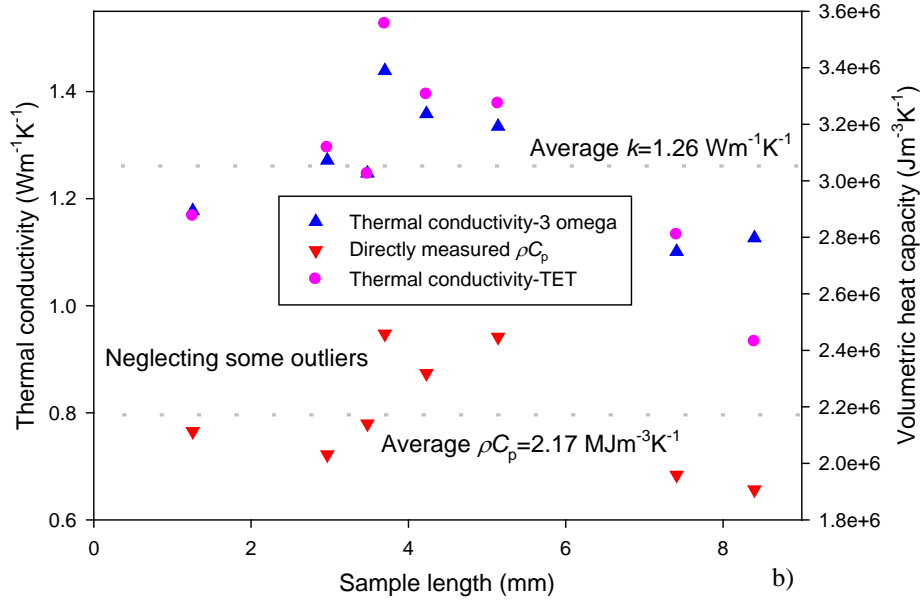
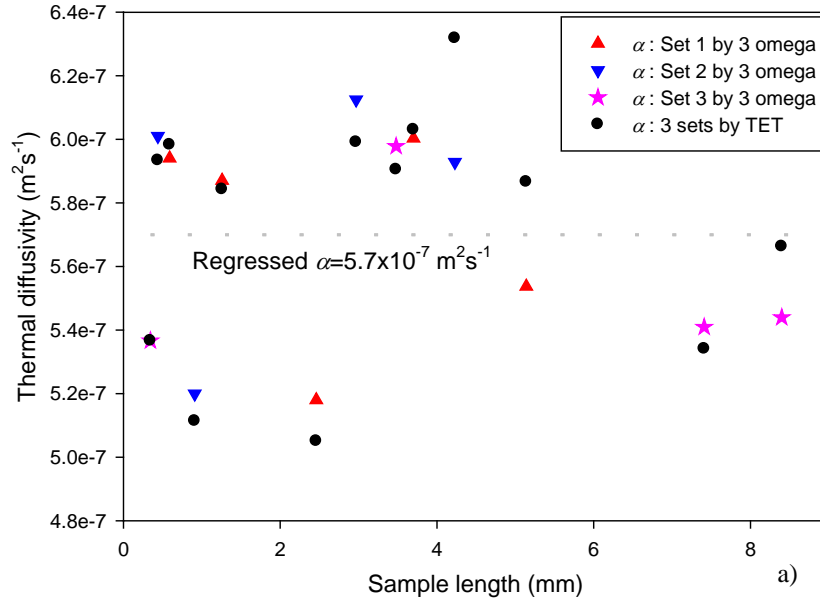
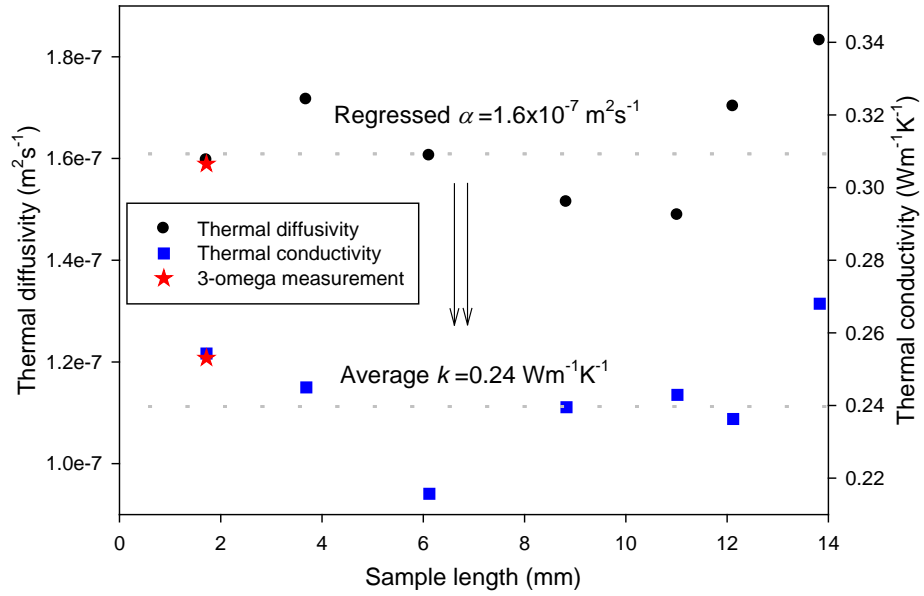


Fig. 5 Thermal conductivity, thermal diffusivity and volumetric heat capacity of the *minor ampullate* silk by the two techniques, a) regression on phase to get diffusivity and radiation effect, b) thermal conductivity by incorporating radiation influence as well as directly measured heat capacity.

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Fig. 6 Thermal property of the as-spun *synthetic silk* by the TET using the ( $\alpha$ ,  $H_e \rightarrow k$ ) method. Additionally, short fiber  $3\omega$  results are shown that have good agreement with the TET results.