Characterizing Thermal Diffusivity of Synthetic Spider Silk using Improved Transient Electrothermal Technique

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ABSTRACT

This paper presents an improved method for measurement of the thermal diffusivity of thin fibers, motivated by the measurement of thermal diffusivity of a synthetically produced spider silk. This synthetic spider silk is being developed for lightweight thermal management applications. The transient/generalized electrothermal technique (TET) has been previously developed to characterize thermal properties, such as thermal conductivity and thermal diffusivity, of thin fibers, but can have significant errors when applied to nanoscale samples. A new, full model was developed to reduce these bias errors by including far-field radiation heat losses, convection heat losses, and non-constant heating effects. The bias errors associated with the original, or reduced, TET model are related to applied currents during experimental measurements of a thin platinum wire. Because the full model requires information about the thermal conductivity of the material of interest, the reduced model should be used as an initial approximation for the thermal conductivity of the fiber to be used in the full model to get a more accurate thermal diffusivity result. This full model can improve characterization of microwires' thermal properties and allows for variations in the process treatments to be more accurately characterized.

Keywords: spider silk, thermal diffusivity, synthetic spider silk, improved characterization model

1 INTRODUCTION

The *N. clavipes* orb-weaving spider produces seven different spider silks, including the strong, elastic dragline silk [1]. Dragline silk is composed of two proteins, MaSp1 and MaSp2. These proteins have highly repetitive sequences which contain distinct modules [2]. These include glycine-rich elastic β-turn spirals (which give elasticity to the fiber – Figure 1a), alanine-rich crystalline β-sheets (which provide strength to the fiber – Figure 1b), and glycine-rich 3_{10} helices [3]. These structures and their modular nature allow spider silk to have such exceptional material properties and have the potential to allow designers to tune the fiber properties based on the constiuent structures in the silk fiber.

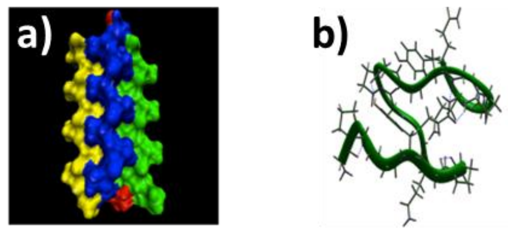

Figure 1. β-sheet module (a), β-spiral module (b).

Because of its favorable properties, spider silk is a much sought after fiber for multiple applications. However spiders cannot be farmed because they are territorial and cannibalistic. To overcome these limitations, many attempts have been made to produce a synthetic spider silk strand based on production and spinning of the various spider silk proteins. Preliminary studies [4] have used transgenic silk worms to produce and spin the fiber with a percentage of the fiber containing spider silk proteins. These chimeric fibers exhibited improved mechanical strength and toughness compared to the native silkworm silk, but didn't have the strength of the natural dragline silk. Another route is to express the MaSp1 and MaSp2 proteins in transgenic sources (tobacco leaves [5] and *E. coli* [6]) and then mechanically spin the proteins into fibers. A microfluidic device was used to spin recombinant silkworm [7] and spider silk [8] proteins into fibers. The fibers had improved properties, especially because they were able to make finer fibers that were similar to the natural dragline fibers. However, the production yield of this approach is low for commercial production. The current study presents preliminary results from synthetic fibers produced from spider silk proteins produced in transgenic goats' milk. The fibers vary by the based on the solutions they pass through as they are spun and the magnitude of stretching during submersion in the solution bath.

Measuring the thermal properties of the synthetic spider silk fibers is significant for two reasons. The first is that natural dragline silk has been reported to have a thermal conductivity and diffusivity comparable to copper, and the magnitude of the thermal properties increases upon stretching [9]. If synthetic fibers can be produced that have similar or improved thermal properties, effective lightweight and flexible heat conduits can be created. The second reason is that the relative magnitude of the thermal properties of the synthetic fiber can be used as a metric to determine the correlation between various processing techniques during fiber production and the quality of the fiber. In order to determine the processing effects, a high precision property measurement must be used, such as the transient electrothermal technique.

2 METHOD

This research uses the transient electrothermal technique (TET) to measure the thermal diffusivity of thin, cylindrical materials [10]. The TET method was developed to measure the thermal conductivity and diffusivity of fine fibers, because of the difficulty in doing this with other techniques such as laser flash [11], 3ω method [12], and microfabrication suspension devices [13]. Additionally the TET method can be applied to both conductive and non-conductive fibers.

In the TET method, the fiber of interest is suspended between two copper heat sinks of sufficient size to provide a constant temperature at the fiber ends (Figure 2a). To reduce electrical and thermal contact resistance, the fiber is affixed with a silver filled epoxy. If the fiber is non-conductive, a thin layer of gold is deposited onto the fiber (Figure 2b), with a preferred resistance on the order of a couple of kΩ. The setup is then placed in a vacuum chamber to reduce the rate of convection (Figure 2c). A constant current is then applied to the fiber to induce uniform Joule heating along its length and the average voltage rise is measured (Figure 2d). The fiber temperature rises, reaching a maximum temperature in the middle of the fiber at steady state (Figure 2e). This voltage rise is due to changes in the resistance of the fiber or gold film caused by the rise in temperature of the fiber.

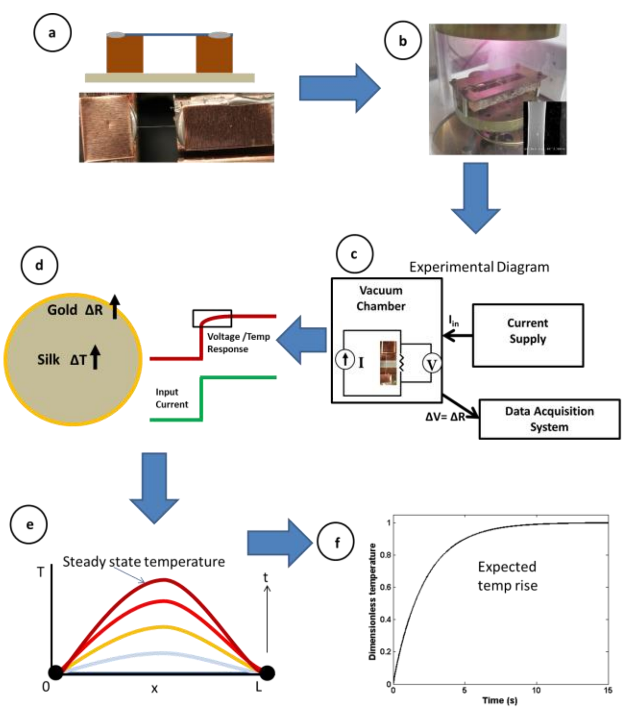

Figure 2. Sample preparation: mounting (a), coating (b), heating and temperature rise (c-f).

To relate this voltage rise to the temperature of the fiber and its properties, the transient, axial heat conduction equation with constant heat generation (q_0''') can be solved (Eq. 1). Because the temperature is not constant along the length of the fiber, the average temperature can be found through integration and normalized by the steady state average temperature. For relatively small magnitudes of temperature increases, the non-dimensional temperature rise is directly related to the measured voltage rise and results in the reduced model for thermal diffusivity, α, as function of fiber length, L, and rise time, t, (Eq. 2), which can be curve fit by means of nonlinear regression to determine the thermal diffusivity (Figure 2f).

$$\frac{1}{\alpha}\frac{\partial \Delta T}{\partial t} = \frac{\partial^2 \Delta T}{\partial x^2} + \frac{q_0'''}{k} \quad (1)$$

$$\frac{\overline{\Delta T}}{\Delta T_\infty} = \frac{\Delta V}{\Delta V_\infty} = 1 - \frac{96}{\pi^4}\sum_{m=1}^{\infty} \frac{e^{-(2m-1)^2 \pi^2 \alpha t / L^2}}{(2m-1)^4} \quad (2)$$

The expression for thermal conductivity, k, is based on the average steady state fiber resistance (R_1), the initial resistance prior to heating (R_0), the applied current (I_1), the temperature coefficient of resistance for the material (α_T), and the diameter (D) and length (L) of the fiber. This reduced model for the conductivity is given in Eq. 3.

$$k = \frac{I_1^{\,2} R_1 L R_0 \alpha_T}{3D^2 \pi (R_1 - R_0)} \quad (3)$$

The underlying principle of the TET method is volumetric heat generation caused by Joule heating, resulting in axial heat flow to constant temperature heat sinks. However, this derivation of the model, which neglects all other forms of heat transfer except for axial conduction and the existence of additional modes of heat transfer, can over-predict the measured property for the case of additional heat losses, and under-predict the measured property for additional heat generation. In order to be used as a valid metric to differentiate fiber processing effects on material properties, a new model (hereafter referred to as the full model) must be used that incorporates radiation, convection, and non-constant heating effects to reduce the bias error of the measured property. Two additional terms are added to Eq. 1 including an effective heat transfer coefficient (Eq. 4), which includes a linearized radiation heat transfer coefficient ($h_r=4\varepsilon\sigma T_0^3$), a convection coefficient h_c, and a non-constant heating correction $I^2R_0\alpha_T$.

$$H_e^{\,2} = \frac{(h_r + h_c)}{Dk} - \frac{4I^2 R_0 \alpha_T}{\pi D^2 L k} \quad (4)$$

Solution of this version of the heat equation results in the full model for thermal diffusivity (Eq. 5), where V_s is the volume of the fiber, and thermal conductivity (Eq. 6).

$$\overline{\Delta T}(t) = \frac{q_0^{'''}}{kH_e^{\,2}}\left[1 - 2\frac{\cosh(LH_e) - 1}{LH_e \sinh(LH_e)}\right] - \frac{8q_0^{'''}L^2}{k}\sum_{n=1}^{\infty}\frac{e^{-\left[(2m-1)^2\pi^2 + (LH_e)^2\right]\alpha t/L^2}}{\left[(2m-1)\pi\right]^4 + \left[LH_e(2m-1)\pi\right]^2} \quad (5)$$

$$\frac{R_1 - R_0}{R_0\alpha_T} = \frac{(I_1^2 - I_0^2)R_0}{V_s kH_e^{\,2}}\left[1 - 2\frac{\cosh(LH_e) - 1}{LH_e \sinh(LH_e)}\right] \quad (6)$$

The current research presents preliminary results of the measured thermal diffusivity for several synthetically produced spider silks by means of the reduced model to show the need for the full model. Then experimental results are shown for platinum wire thermal properties measurement by means of both the reduced and full model to show reduction of error when measuring with the full model.

3 RESULTS

To produce the synthetic spider silk fiber, a protein dope solution is extruded through a needle into a pure isopropanol (IPA) bath where it coagulates into a fiber. This fiber is then drawn and stretched into another bath of an IPA and water solution. After leaving this bath, some fibers are then dipped into a pure water bath. A Caucasian female hair and five different synthetic fibers produced in this way were tested: an as spun fiber with no solution treatments (Synth #1), an 80:20 IPA/water solution with a 2X stretch (Synth #3), an 80:20 IPA/water solution with a 3X stretch and water dip (Synth #3), an 50:50 IPA/water solution with a 2X stretch (Synth #4), an 50:50 IPA/water solution with a 2X stretch and water dip (Synth #5). The preliminary results from these measurements are given in Figure 3, with the uncertainty representing 10% of the measured value expected by the method according to Guo [10]. It is uncertain if the variation in the thermal diffusivity amongst the different type of synthetic fibers is because of the process treatments or from the measurement bias.

To verify that the full model reduces uncertainty in thermal diffusivity measurement, platinum wires at various lengths were tested. Figure 4 shows the deviation of the measured diffusivity compared to the literature value [14], based on the reduced model, the full model only including non-constant heating, the full model only including radiation, and the complete full model. The results show that the full model greatly reduces the error in the measured thermal diffusivity. At higher currents where radiation effects become increasingly non-linear, the full model is no longer valid and the error increases, although its magnitude is still lower than the other models.

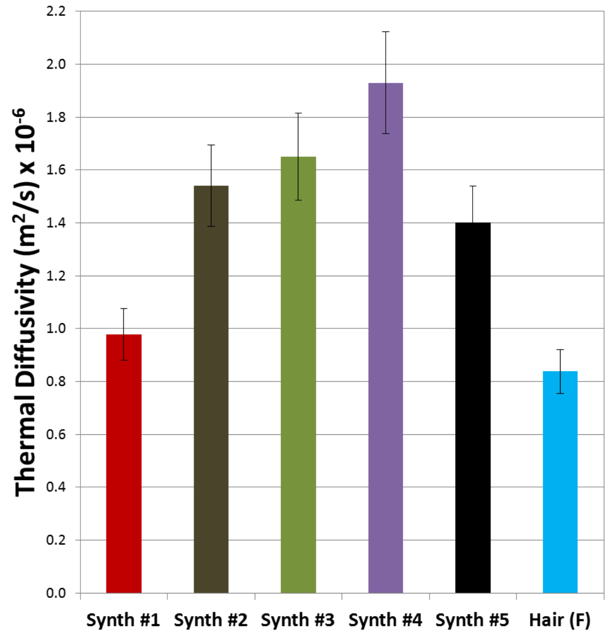

Figure 3. Prelimiary results of the thermal diffusivity of synthetic spider silks of various processing treatments. Uncertainty bars represent10% uncertainty by the TET method.

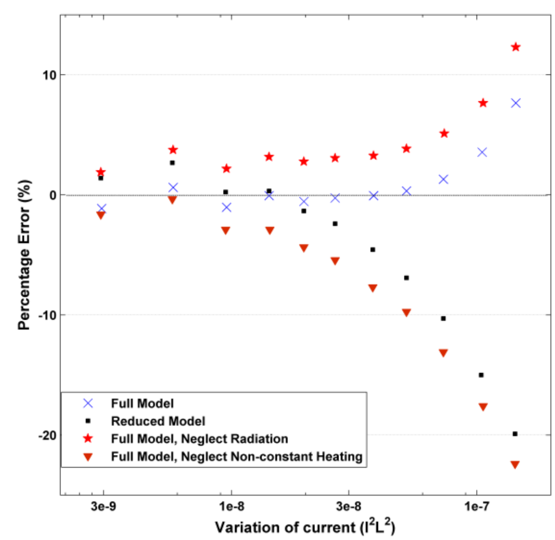

Figure 4. Error of platinum thermal diffusivity measurement based on different models.

With these successful results with platinum, the full model needs to be applied to synthetic spider silk fibers after the temperature resistance relationship of the gold coated fibers is successfully measured.

4 CONCLUSIONS

The conclusions of this research are:

- The newly developed full model can improve the measurement of the thermal diffusivity of thin fibers, as verified by experimental tests with platinum wire
- This improve accuracy can be used to correlate the effect of various process treatments on sythetic silk production

5 ACKNOWLEDGEMENTS

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