ENGINEERING PROPERTIES OF SPIDER SILK

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ABSTRACT

Motivated by the high level of strength and toughness of spider silk and its multifunctional nature, this paper reports on the engineering properties of individual fibers from Nephila Clavipes spider drag line under uniaxial tension, transverse compression and torsional deformation. The tensile properties were compared to the Argiope Aurentia spider silk and show different ultimate strength but similar traits of the unusual combination of strength and toughness characterized by a sigmoidal stress-strain curve. A high level of torsional stability is demonstrated. comparing favorably to other aramid fibers (including Kevlar fibers).

INTRODUCTION

Strength and toughness are usually considered mutually exclusive properties for materials. In spite of the progress made in the recent years in polymeric fiber science and technologies, the search for a truly strong and tough fiber continues. It is of practical and scientific interest to explore the limit of strength and toughness of fibrous materials; and to examine the factors which contribute to the development of a combination of strength and toughness in materials. The answers to these questions may be found in nature.

In the world of natural fibers, spider silk has long been recognized as the wonder fiber for its unique combination of high strength and rupture elongation. An earlier study indicated spider silk has strength as high as 1.75 GPa at a breaking elongation of over 26%.[1,2]. With toughness more than three times that of aramid and industrial fibers, spider silk continues to attract the attention of fiber scientists and hobbyists alike. [3-13]

Considering the remarkable mechano-chemical properties of spider silk and fueled by the recent progress in biotechnology, there is a revival of interest in using spider silk as a model for the engineering of high energy absorption fibers [14]. Because of the fineness of spider silk, on the order of 4 µm, the characterization of the mechanical properties of spider silks are limited to tensile mode. Little is known about the response of spider silks to other modes of deformation in the transverse direction and in torsion. Original data are presented on the tensile, transverse compression and torsional stress-strain properties of the spider silk from Nephila Clavipes spiders. This was made possible by using an ultra sensitive micromeasurement fiber testing system developed by Kawabata [15]. From these experimental data, the engineering properties: tensile modulus, transverse compressive modulus, and shear modulus of the spider silk was determined.

TENSILE PROPERTIES

The drag line of an Argiope Aurentia spider was forcibly silked and prepared for tensile testing according to the procedure of Work [16]. One of the outstanding characteristics of spider silk is its fineness. For example the drag line is between 3-4 microns in diameter. The cribellate silk was found to be as fine as 0.03 µm in diameter. Scanning electron microscope pictures indicated that the drag line silks have a circular fiber cross-section. Table I presents the diameter of spider drag line silk in comparing to other textile fibers.

TABLE I. Diameter of Spider Silk and Other Reference Fibers

	Linear Density(tex)	Diameter Mean value (□m)	Coeff. Variation (%)
Spider Silk	0.014	3.57	14.8
B. mori Silk*	0.117	12.9	24.8
Merino Wool	0.674	25.5	25.6
Polyester Filament	0.192	13.3	2.4
Nylon 6 Filament	0.235	16.2	3.1
Kevlar 29	0.215	13.8	6.1

* In the case of B. mori silk, diameter shows means of bottom and height on the triangle shape.

Before testing, each specimen was examined under the microscope to insure that only single fibers were used. The diameter of the Argiope Aurentia spider drag line measured by scanning electron microscopy was 3.1 microns which corresponds to 0.085 denier assuming a fiber density of 1.25 gm/cc.

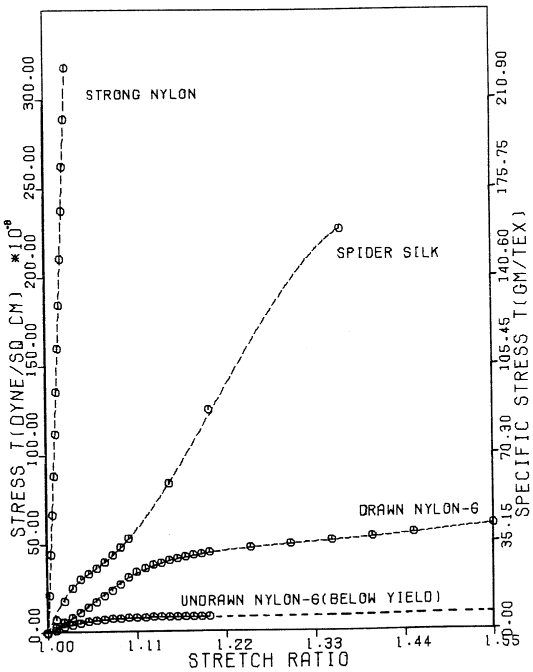

FIGURE 1. Tensile Stress-Strain Curves of Spider Silk and other Polyamide Fibers

The stress-strain curve of the spider silk assumes a sigmoidal shape similar to that of an elastomer, demonstrating a well balance of strength and elongation at 1.75 GPa (15.8 g/den) and 36%, respectively. This "rubber-like" stress-strain curve is characterized by three distinct regions: Region I (0-5%) is characterized by a high initial modulus of 34 GPa; Region II (5-21%) shows a pseudo yield point at 5 % before strain hardening to a maximum modulus of 22 GPa at 22% elongation and Region III (21-36%) exhibits a gradual reduction of modulus until reaching failure strength of 1.75 GPa. at 36% elongation. An examination of the area under the stress-strain curves shows a toughness level of 2.8 g/denier. This is much higher than the toughness of the aramid fiber (0.26 g/denier) and nylon 6 fiber (0.9 g/denier)

The material properties of spider silk vary from specimen to specimen, as demonstrated in our past studies of the Nephila Clavipes spider. The silk from a Nephila Clavipes spider obtained from the US Army Natick RD&E Laboratories was tested in the micro-tensile tester at Professor Kawabata's laboratory. The spider silk was tested by simple elongation at a strain rate of 100% per minute using a gage length of 1.25 cm. Additionally, transverse compression, torsional properties of the Nephila Clavipes spider silk were also tested under ambient and wet conditions.

Ten (10) replications of the Nephila Clavipes spider drag line silk were made to generate the average tensile stress-strain curve shown in Figure 2. wherein a sigmoidal shape stress-strain curve similar to that of the Argiope Aurentia spider is shown. With an average initial modulus of 12.71 GPa. the failure stress of the fiber is 0.85 GPa at 20% breaking elongation. Obviously, the Nephila Clavipes spider makes a less strong and tough silk than the Argiope Aurentia spider.

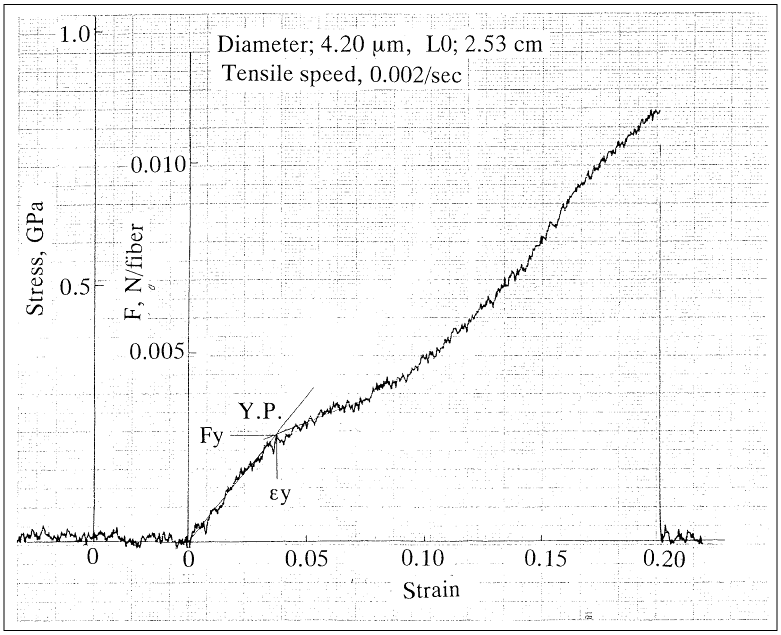

FIGURE 2. Tensile Property of Single Fiber

In comparison with the other textile fibers , as shown in Figure 3, the Nephila Clavipes spider silk provides the best balance of strength and toughness.

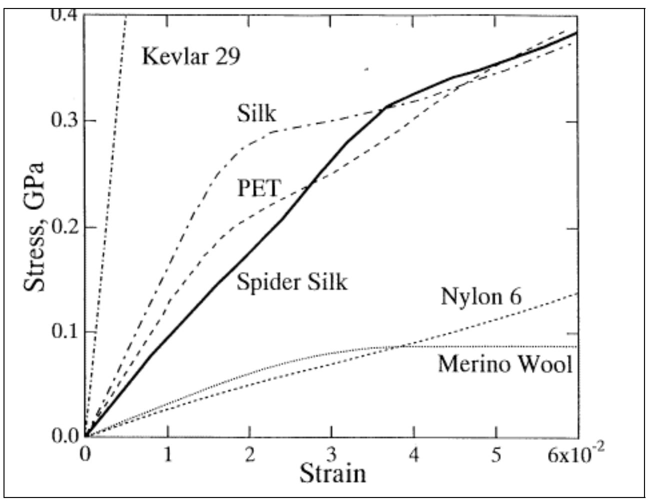

FIGURE 3. Tensile stress-strain behavior of N. Clavipes spider silk compared to other textile fibers

TRANSVERSE PROPERTIES

The compression tests in the transverse fiber diameter direction were carried out by placing a single fiber between a flat and mirror-finished steel plate and a mirror finished 0.2 mm square compression plane. Because of the fineness of the spider fiber, a combination of sensitive instrumentation and mechanistic analysis are required in order to assure accurate measurement of the compressive stress-stain properties.

The Nephila Clavipe spider silk fibers were subjected to transverse cyclic loading at a compressive speed of 0.3 cm/s. under ambient and wet conditions, The compressive modulus of the fiber tested in ambient condition was 0.58 GPa. and the fiber experienced a high degree of permanent deformation (~20%). As shown in Figure 4, the ability of spider silk to resist transverse compression is lower than all the other textile fibers, indicating a high level of anisotopy .

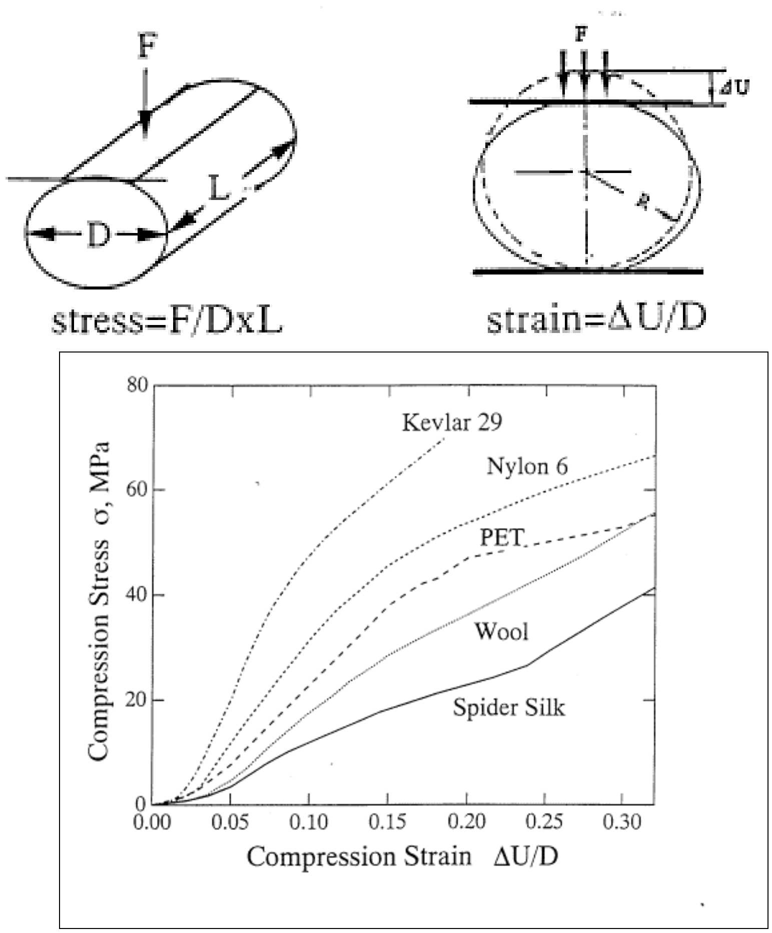

FIGURE 4. Compressive stress-strain behavior of N. clavipe spider silk

TORSIONAL PROPERTIES

Through torsional testing, the shear modulus of a fiber can be determined. The torsional behavior of the N. clavipe spider silk was characterized with an ultra-sensitive Kawabata torsional tester. As shown in Figure 5, a single fiber having both ends reinforced by a paper backing using ceramic adhesives is hung on a top hook connected to a highly sensitive torque detector supported by two torque wires made of 0.2 mm piano wire. The bottom end is connected to a bar, and both ends of the bar are inserted into slits of a servo-driven cylindrical tube. The full scale of the torque meter is 0.0025 gf-cm/10 volt. A high level of torsional resistance is observed for the spider silk. The shear rigidity, as determined from the torque-deformation diagram shown is Figure 6, is 2.38 GPa. that is higher than all the other textile fibers including Kevlar 29. This appears to be consistent with the intended use of the drag line - as a life line for the spider (as in a mountain climbing rope) which requires a high level of torsional stability.

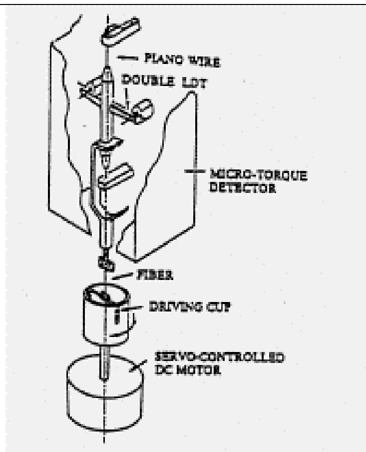

FIGURE 5. Torsion tester for single fiber

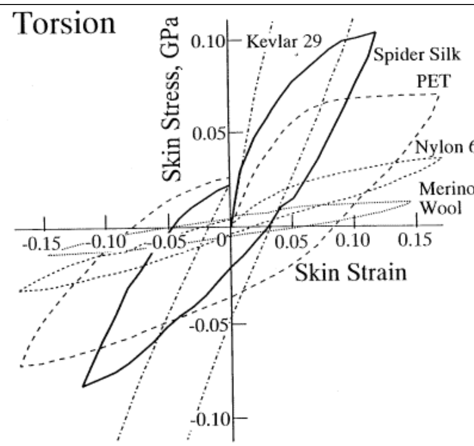

FIGURE 6. Torsional stress-strain behavior of N. clavipe spider silk

SUMMARY AND OBSERVATIONS

The mechanical properties of the drag line silk of Argiope aurentia and N. clavipe spider were examined. The engineering properties of N clavipe spider was characterized under tensile, transverse compression and torsional loading. Table II provides a summary of the engineering properties of the spider silks in comparison with other natural and synthetic polyamide fibers.

TABLE II. Engineering Properties of Polyamide Fibers

	E_L (GPa)	E_T (GPa)	G_L (GPa)	E_L/E_T	E_L/G_L
Argiope aurentia spider silk	34.00	-	-	-	-
N. clavipe Spider Silk	12.71	0.579	2.38	21.95	5.34
B. Mori Silk	9.90	-	3.81*	-	4.93*
Merino Wool	3.50	0.93	1.31	3.76	2.67
Nylon 6 Filament	2.71	1.01	0.52	2.68	5.21
Kevlar 29	79.80	2.59	2.17	30.81	36.77

Although the two spiders do produce silks with different properties, they both demonstrate a unique combination of strength and toughness which are quite essential for withstanding foreign object bombardment and absorbing the impact energy generated by insects colliding with and becoming ensnared in the web. Another outstanding characteristic of spider silk is its high level of shear rigidity compared to industrial fibers. Torsional stability is essential in order for the spider's drag line to serve as a life line for the spider in thin air.

With strength close to 2 GPa; stiffness of up to 30GPa and high elongation at break of over 30%, the spider seems to be capable of processing silk effortlessly through solution spinning, transforming protein liquid to non-water soluble fiber under ambient temperature. The spinning process can be carried out in air or under water, producing silks having a wide range of properties and extreme fineness, from 0.01-4 µm. This remarkable fiber is also very durable and can resist degradation in a wide variety of environments. Through special enzyme digestion, the spider also recycles its silk on a daily basis. Accordingly, spider silk is clearly an example of a multifunctional fiber that plays a key role in insect ecology and serves as an excellent model for the flexible manufacturing of the next generation of specialty fibers.

REFERENCES

[1] Zemlin, J. C., A Study of the Mechanical Behavior of Spider Silks, U. S. Army Natick Report AD 333, 19 .

[2] Ko, Frank, Nonlinear Viscoelasticity of Aramid Fibers, Ph. D Thesis, Georgia Institute of Technology, Atlanta, Ga, 1977.

[3] Witt, P. N., C. F. Reed, and D. B. Peakall, A Spider's Web: Problems in Regulatory Biology, Springer-Verlag, New York, l9b .

[4] Friedrich, V. L. Jr., and R. M. Langer, "Fine Structure of Cribellate Spider SiIk", Am. Zoologist. 9, 91 (1969).

[5] Peakall, D. B., "Synthesis of Silk, Mechanism and Location", Am. Zoologist, 9, 71(1969)

[6] Lucas, F., J. T. B. Shaw, and S. G. Smith, "Comparative Studies of Fibroins: I. The Amino Acid Composition of Various Fibroins and Its Significance in Relation to Their Crystal Structure and Taxonomy", J. of Molecular Biology, 2, 339(1960).

[7] Warwicker, J. 0., "Comparative Studies of Fibroins", J. Molecular Biology, 2, 350(1960).

[8] Marples, B. J., "The Spinnerets and Epiandrous Glands of Spiders", J. Linnean Soc. (Zoology), 46, 209(1967).

[9] Wilaon, R. S., "The Structure of the Dragline Control Valves in the Garden Spiders", Quart. J. Micr. Sci., 104, 549(1962).

[10] Wilson, R. S., "The Control of Drag Line Spinning in the Garden Spiders", Quart. J. Micr. Sci., 104, 557(1962).

[11] Wilson, R. S., "Control of Drag-line Spinning in Certain Spiders", Am. Zoologist, 9, 103(1969).

[12] Lucas, F., J. T. B. Shaw, and S. G. Smith, "The Chemical Constitution of Some Silk Fibroins and Its Bearing on their Physical Properties", J. Textile Inst., 4, T440 (1955).

[13] Levi, H. W., L. R. Levi, and H. S. Zim, A Guide to Spiders, Golden Press, New York, 1968.

[14] Kaplan, D., Adams, W. W., Famler, B., and Viney, C., editors, Silk Polymers: Materials Science and Biotechnology, .ACS Symposium Series 544, American Chemical Society, DC, 1994

[15] Kawabata, S., Micromeasurement of Mechanical Properties of Single Fibers, PP. 311328,

[16] Work, R. W., Personal communication.

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