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Some Significant Research Insights on Spider Silk

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Abstract

The article surveys some recent research works on spider silk. The engineering properties of individual fibers from Nephila Clavipes spider drag line under uniaxial tension, transverse compression and torsional deformation has been reported. A high level of torsional stability is demonstrated. Comparing favorably to other aramid fibers (including Kevlar fibers). The length and width of four different types of webs like orb web, funnel web, dome web and irregular mesh web have been measured and also the width of the single silken thread of the four spider webs measured. The mechanical properties of different type web threads were studied by measuring the width of the single thread using micrometry. The width of the prey capture thread was found to be higher in the orb web. The width of the egg sac thread was higher in the dome web and orb web. The length and width of different types of web were measured. The higher length of different types of web was found in orb web. We found that the orb webs were stiffer and stronger. These findings yield insight into the strength of the capture threads. Spider silk produces biomaterials that exceed manufactured materials with extraordinary characteristics. SS-fibers are as tough as steel and some SS-fibers have elasticity near caoutchouc.

Keywords: Spider silk, mechanical properties, Web, Biomaterials

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 a like [3-13].

Silk is used by spiders in dispersal in different ways. One method, bridging, is to cast a line into the breeze and, when it catches on a distant object, to climb out on the line to its end. Bridging may also be accomplished by dropping on a line and swinging on it to reach a new site [14]. Silk is a fibrous protein secreted by labial glands in Lepidoptera, Hymenoptera or by accessory tubes of the genital organs of hydrophilus, by tarsal glands of Embioptera and Embidae, and by malpighian tubes of certain blatella, a variety of insects and arachnids [15].

The native protein of silk gland "fibrinogen" is water soluble, while passing through the spinnerets it becomes a tough insoluble product "fibroin" in which the molecule assume an orderly crystalline arrangement in the long axis of the fiber. The silk, which is coated with sericin, a glue like proteins that hold the fibroin core together. The silk fibers have been used for decades as sutures in biomedical application and have potential as scaffolds in tissue engineering [16-19]. Spiders also actively modify the architectures of webs in response to predators and prey [20]. Thus, studying architectures of spider webs can give us insight into how spiders confront selective pressures in their environment some aspects of webs can be difficult to measure accurately in the field so that formulaic estimators are instead employed [21]. Spiders in the genus *Argiope* often decorate their nearly invisible orb webs with conspicuous zigzags of silk called stabilimenta. However, the ecological function of stabilimentum building is still unresolved [22].

Because of its reflectivity in both the visible and ultraviolet (UV) regions of the spectrum [23], many authors have suggested that the stabilimentum is used as a visual signal. However, it is much debated whether the primary recipients of this signal are predators, prey or mega fauna. Arguments that the primary recipients are predators suggest the stabilimentum thwarts predators by displacing attacks or changing the apparent size or shape of the spider [24,25].

Some insects have evolved over millions of years to produce fantastic biomaterials and sometimes they exceed manufactured materials with extraordinary characteristics. One of these biomaterials is spider silk (SS) that contains large proteins. SS-fibers are as tough as steel and some SS-fibers have elasticity near caoutchouc [26,27]. When one combines their fantastic characteristics, SS show double or even triple toughness of manufactured-fibers such as Kevlar or Nylon. In addition, SS shows (I) passive-inflammation, (II) it is inactive for allergic reactions, (III) it is completely biodegradable-material, (IV) it is hypoallergenic and (v) it is antimicrobial at ambient conditions [28]. These properties present SS as a future biomaterial. Therefore, this article draws attention to the importance of SS for different applications and shows the structure function close relation between the highly repetitive (HR) SS-proteins with the corresponding conformational alteration to strings from the initial solution form. This information is decisive because one has to know the mechanism (s) how this alteration occurs and to understand the intrinsic characteristics of SS-fibers. In addition, it is important to know the highly sophisticated assembly techniques of silk proteins.

Engineering Properties of Spider Silk

Tensile properties

The drag line of an Argiope Aurentia spider was forcibly silked and prepared for tensile testing according to the procedure of Work [29]. 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. 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.

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 was 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. 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.

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 anisotropy.

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 gfcm/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.

Mechanical Properties

Width

The mechanical properties of different type web threads were measured by taking the width of the single thread using micrometry measured and showed in Table 2. The width of the prey capture thread was found to be higher in the orb web (24 µm ± 3.03) followed by dome web (14.22 µm ± 2.59), irregular web (11.94 µm ± 0.36) and funnel web (11.89 µm ± 0.62). The width of the egg sac thread was found to be higher in the dome web (14.92 µm ± 1.02) followed by orb web (14.04 µm ± 1.18), irregular web (12.75 µm ± 0.45) and funnel web (11.38 µm ± 0.39) shown in Table 3.

The width of the web thread was found to be higher in the orb web (35.83 µm ± 4.40) followed by dome web (30.02 µm ± 3.68), irregular web (28.97 µm ± 3.41) and funnel web (14.94 µm ± 2.47) shown in Table 4. The length and width of different types of web has been measured and showed in Table 5. The higher length of different types of web was found in orb web (39.90 ± 1.28) followed by funnel web (30.70 ± 2.18), dome web (29.50 ± 1.45) and irregular web (28.60 ± 1.41). The higher width of different types of web was found in funnel web (31.90 ± 0.76) followed by orb web (31.60 ± 1.98), irregular web (23.10 ± 1.09) and dome web (17.80 ± 0.69).

Different types of spider webs include: Spiral orb webs, Funnel webs, Dome or tent webs, Irregular web. Some webs will have loose, irregular tangles of silk above them. These tangled obstacle courses serve to disorient and knock down flying insects, making them more vulnerable to being trapped on the web below. They may also help to protect the spider from predators such as birds and wasps. During my present investigation, I have been recorded four types of web namely orb web, doom web, funnel web, irregular web. It shows the diversity of different types of web in an agro ecosystem. From the total number of webs observed the orb web (38%] occupies a dominant position in the occurrence in the field of agro ecosystem, because these orb webs has a potential of predatory character.

Some Investigations of Spider Silk Properties

During the present study four different types of webs have been observed. Three different families of spider have been observed namely Araneidae, Lycosidae and Eresidae, which has built different types of web. The higher percentage of different type of webs recorded in orb web (38%) followed by funnel web (25%), dome web (21%) and irregular web (16%) which is shown in Table 1.

S. No	Family Types of web Total no. of web (%)
1	Araneidae Orb web 38
2	Araneidae Dome web 21
3	Lycosidae Funnel web 25
4	Eresidae Irregular mesh web 16

Table 1: Percentage of webs recorded in the study area during September, 2010 – February, 2011.

Different types of spider webs include: Spiral orb webs, Funnel webs, Dome or tent webs, Irregular web. Some webs will have loose, irregular tangles of silk above them. These tangled obstacle courses serve to disorient and knock down flying insects, making them more vulnerable to being trapped on the web below. They may also help to protect the spider from predators such as birds and wasps [30]. During my present investigation, I have been recorded four types of web namely orb web, doom web, funnel web, irregular web. It shows the diversity of different types of web in an agro ecosystem. From the total number of webs observed the orb web (38%) occupies a dominant position in the occurrence in the field of agro ecosystem, because these orb webs has a potential of predatory character.

Tailored spider silk for biomaterials

There are different types of SS-webs (SSWs); among the most famous is the orb-web (OW) that contains different sorts of SS [31]. In general, components of orb-web are made of very robust SS. The major ampullate (MA) glands produce two different types of protein. As a particular case, MA-SS can be utilized as roping thread that can help to escape predators. For example, the catch winding of an OW contains strings with one sort of protein that is generated in the gland of spider as flagella form (Flag). Flag-SS has high degree of elasticity about three hundred percent which is completely enough to squander the internal energy of prey. The web scaffolding joint-points are well welded to external supports (such as trees for example) through advanced silk binder contain special proteins created in the insect [32,33].

The structure of spider silk

Essentially, SS contains special proteins, which consists of huge amounts of hydrophobic-amino acids (for example glycine and/or alanine) and nonpolar amino acids, and there is no tryptophan. SS-protein exhibits a chemical composition very close to amino acid with highly repetitive amino acid sequences that composes about 90% of the entire SS-protein. In addition, there are short polypeptide stretches having nearly 10-50 amino acids. Each repeat of them has functional characters leading to the wonderful mechanical properties of SS-threads. In particular, MASS contains up to four typical oligopeptide motifs that suffers different repetition as {i} GGX (X=A, S or Y) {ii} (GA)n/(A)n, {iii} GPGGX/GPGQQ and {iv} regulated-space successions that have charges on their amino acids. Scheibel et al. [34] have shown that some repetitive domains and some non-repetitive domains are present at the ends of protein's series. The non-repetitive termini control the processes of the proteins assembly of SS-protein into fibers [35].

Rising et al. have shown that the regions comprise some hundreds of amino acids and they reported that well located and defined tripartite and tripartite-forms are present in sol. Several authors [36,37] reported that these domains result in some inter-molecular disulfide bonds, which, under oxidizing conditions, can stabilize dimers and multimers. As a consequence, several papers reported that these domains can lunch and appoint texture of SS-proteins.

The texture of spider silk

Dicko et al. [38] have shown that assembly process cannot initiate with globular folded protein monomers. It can start essentially with unfolded proteins at very high concentrations. In order to keep and maintain high concentrations of protein, Hijirida et al. [13] have reported that several mechanisms should be necessary to keep these high concentrations as high as up to fifty percent w/v [39] inside the insect. This includes lyotropic liquid crystallinity, glycosylation of the external superficies of the tucked SS-proteins and period split persuade by a polyol or by a phospholipid surfactant. SS transforms to texture when starting the spinning duct and the silk form turns H2O-resistable [40]. Different conditions such as pH, ionic concentration, water content, etc. should be controlled to get good and efficient assembly. This demands bi-stable bending processes of the concerned protein and firm control of the surrounding states.

Mimicking nature-recombinant spider silk

Authors have used different techniques for recombinant producing SS-proteins, because recombinant production of ample quantities of SS-proteins is crucial to clarify and to understand their assembly behavior and their structure [41-43]. It is very complicated to characterize the exact cDNA successions of a SS-gene because of its highly repetitive character of individual SS-molecules. The conversion of premier or fractioned silk genes to steward of some microorganism bacteria can lead to get recombinant SS-proteins. However, bacteria are not the suitable host for this task because the genes have large size [44]. In addition, when one compares the various codon uses of spiders with bacteria, one can note that the recombinant creation of SS-proteins in bacteria is more hard and difficult [45].

Artificial spinning of spider silk

It is worth pointing out that researchers will be able, in the near future, to understand and test the texture of SS-threads in a functional in vitro weaving technique due to the availability of recombinant SSproteins. Figure 2 illustrates that the produced SS-string looks like natural silk in its mechanical properties, fine-, and chemical-structure [46]. In order to adapt the developed spinning machinery of spiders, different parameters should be considered:

First, in addition to the phase separation process in the spinning duct and the protein composition of the spinning dope, one should consider several mechanical parameters silk assembly. For example, spiders, in nature, use the weight in case of curling and draw the thread with the hind legs out of the spinning wart [47]. In laboratory, scientists copied this drawing process by forced silking of captive spiders. It is worth noting that researcher have reported important differences in thread diameters, ductility and resilience depending on temperature and spinning speed [48]. Several papers reported that SS obtained at higher groggy quickness have a little bit more output. However, they are less extendable and feebler than SS interweaved at reduced speeds. In order to weave recombinant spider silk proteins for scientific objectives, one should consider some aspects: First, researchers can utilize wet-spinning processes [49] and they can use silicon tinny spinnerets (on microscale) some meters of insect or SS-string. These processes will lead to wet-spun silks with radius with ten times more than the radius of normal SS, which lowers the mechanical properties.

Researches can use special posts-pinning techniques that can lead to silks having better radius [50]. In all cases, so far, the mechanical characteristics gained by synthetic weaving techniques are by far thinner than that of normal SS [51]. SS-proteins, in nature, are exclusively transform into SS-threads. It is possible, in vitro, that SS-proteins transform in other two- or three-dimensional forms. One can notice from the images of electron microscopy different forms as: Capsule, sphere, thread and nano-fibrils, in addition to a hydrogel and a film (image) formed by recombinantly generated tailored SS-protein [52]. One can exceed nature when using SS in three dimensions. Figure 3 shows SS-protein with three dimension microscopic structures. Recently, scientists attempt to use SS-protein as biopolymer (novel biomaterial) for different applications. For example, researchers can prepare SS-films from a watered SS-sol [53].

Here, researchers can pour a solution of SS with suitable solvent such as water and let it to evaporate. Then the SS-protein textures on the surface and shape a transparent, robust diaphragm. One can tailor the thickness of films from some nanometers up to different μm's having several mechanical and chemical properties. This can occur with good choice of temperature, solvent and surrounding conditions. Here, the produced films can give secondary and tertiary structure formation of these proteins depending on preparation conditions. Several papers [54,55] reported that SS-proteins of MA are intrinsically unfolded in aqueous solution. However, if one prepares a SS-film, the proteins rapidly will alter to a spiral arrangement and post-handling of the diaphragms with non-polar solvents such as methyl alcohol can lead to more structural rearrangements of SS-protein. This can increase the beta-sheet content dramatically. Moreover, SS, in vitro, can further able to self-assemble into small nano-fibrils upon developing, at room temperature for some days, in potassium phosphate buffer. One can structurally compare the obtained SS-fibrils with amyloid fibrils.

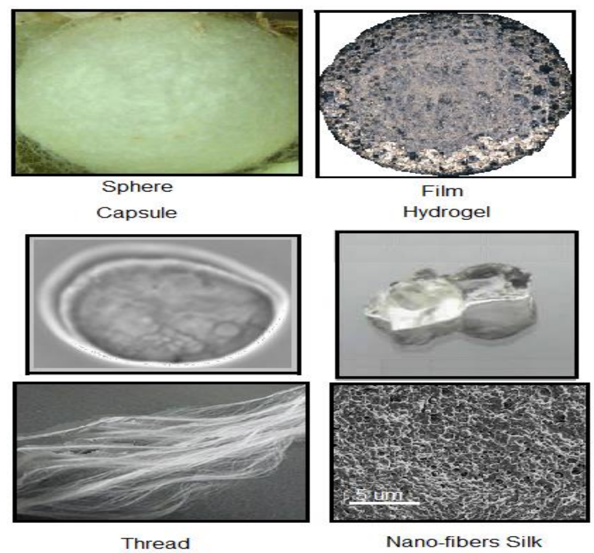

Figure 1: Various forms of spider silk [56].

Interestingly, testing the composition-function correlations of SSproteins in the near future will explain the reason of extreme toughness of SS-threads, in addition it will help to tailor and even design new polymeric biomaterials. In summary, to discover the secrets behind the extraordinary toughness of SS-threads researchers should take more deep steps to analyze the structure-function relationship of SS-proteins which will also help to tailor, engineer and design novel bio- and polymeric-materials. Moreover, the control of SS-assembly will help researches to obtain new biomaterials tailored to have characteristics under desire upon the market demand [56].

Conclusion

The mechanical properties of the drag line silk of Argiope aurentia and N. clavipe spider were examined. The engineering properties of N clavipe spider were characterized under tensile, transverse compression and torsional loading. 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.

Knowledge about molecular biology of spider silk and silk network structure is growing rapidly and provides a rational basis for the design of structural materials through genetic engineering. In the present work the mechanical properties of four different type of web's has been analysed to know their mechanical properties. From the analysis it shows that the orb web contains much width and elasticity when compared with other types of webs. Similar kind of work in mechanical properties was done by [3]. By analysing the mechanical property one can know its strength and how far one can use this spider web as a substitute for other synthetic silk fibers.

One can structurally compare the obtained SS-fibrils with amyloid fibrils. Interestingly, testing the composition-function correlations of SS proteins in the near future will explain the reason of extreme toughness of SS-threads, in addition it will help to tailor and even design new polymeric biomaterials. In summary, to discover the secrets behind the extraordinary toughness of SS-threads researchers should take more deep steps to analyze the structure-function relationship of SS-proteins which will also help to tailor, engineer and design novel bio- and polymeric-materials. Moreover, the control of SS-assembly will help researches to obtain new biomaterials tailored to have characteristics under desire upon the market demand.

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