

## Tailored Spider Silk: The Future Solution to Biomaterials

Abdalla S\*, Obaid A, Al-Marzouki F and Bahabri F

Department of Physics, Faculty of Science, King Abdulaziz University Jeddah, P.O. Box 80203, Jeddah 21589, Saudi Arabia

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 [1,2]. 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 [3]. 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. There are different types of SS-webs (SSWs); among the most famous is the orb-web (OW) that contains different sorts of SS [4]. 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 [5,6].

### 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 [7]. As it is illustrated in Figure 1A, 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 (Figure 1B). 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, MA-SS contains up to four typical oligopeptide motifs that suffers different repetition as {i} GGX (X=A, S or Y) {ii} (GA)<sub>n</sub>/(A)<sub>n</sub>, {iii} GPGGX/GPGQQ and {iv} regulated-space successions that have charges on their amino acids (Figure 1C) [5,6]. Scheibel et al. [8] have shown that some repetitive domains and some non-repetitive domains are present at the ends of protein's series [8]. The non-repetitive termini control the processes of the proteins assembly of SS-protein into fibers [9]. 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 [9].

Several authors [10,11] 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

[10,11] reported that these domains can lunch and appoint texture of SS-proteins [10,11].

### The Texture of Spider Silk

Dicko et al. [12] have shown that assembly process cannot initiate with globular folded protein monomers. It can start essentially with unfolded proteins at very high concentrations [12]. 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 [13] 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 H<sub>2</sub>O-resistable [14]. Figure 2 illustrates this situation. 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 recombinantly 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 [15-18]. 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 [19]. 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 [20].

### Artificial Spinning of Spider Silk

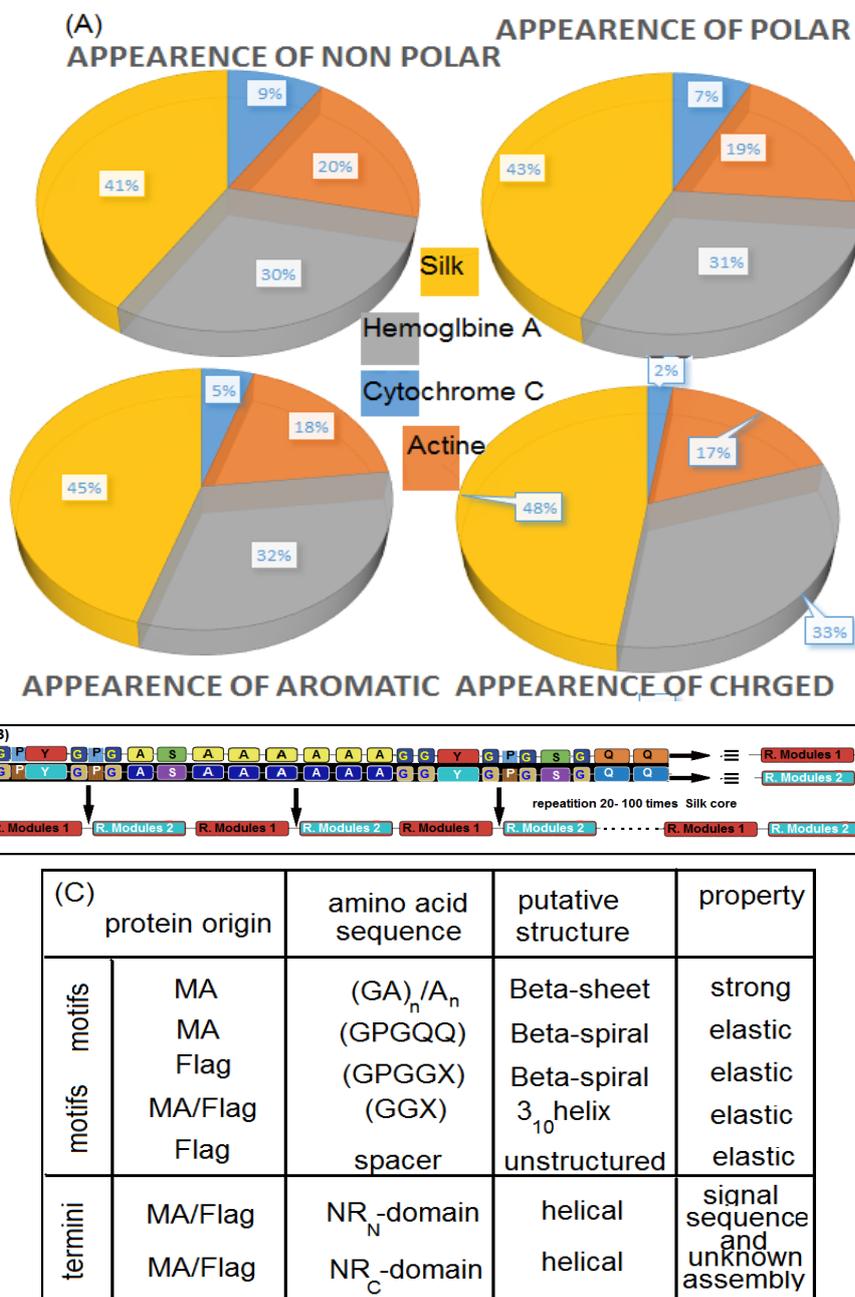
It is worth pointing out that researchers will be able, in the near future, to understand and test the texture of SS-threads in a functional in vitro weaving technique due to the availability of recombinant SS-proteins. Figure 2 illustrates that the produced SS-string looks like natural silk in its mechanical properties, fine-, and chemical-structure [21]. In order to adapt the developed spinning machinery of spiders, different parameters should be considered:

\*Corresponding author: Soliman Abdalla, Department of Physics, Faculty of Science, King Abdulaziz University Jeddah, P.O. Box 80203, Jeddah 21589, Saudi Arabia, Tel: +966-58-234-3822; E-mail: [smabdullah@kau.edu.sa](mailto:smabdullah@kau.edu.sa)

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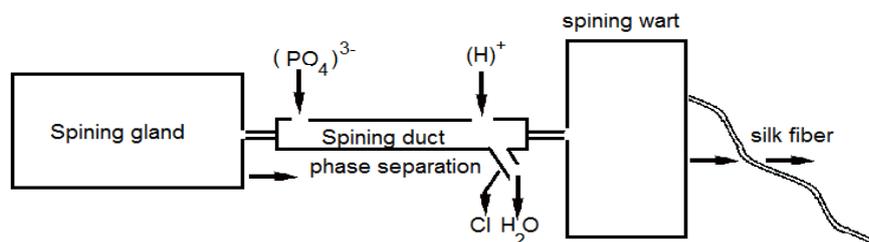
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**Figure 1:** (A) Comparing three well-known proteins amino acids to SS. (B) Proposed pattern of the constructing of a major ambulate (MA) SS-protein. (C) Amino acid motifs of SS-proteins. Amino acids present in MA and Flag silk are restored with their delusive composition and their influence on the ultimate characteristics of the string.

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 [22]. 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 [23]. Several papers reported that SS obtained at higher groggy quickness have a little bit more output. However, they are less extendable and more feeble 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 [24] 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 [25]. In all cases, so far, the mechanical characteristics gained by synthetic weaving techniques are by far thinner than that of normal SS [26].



**Figure 2:** The spinning gland secretes and stores highly concentrated SS-protein solution. Then, the phase separation process occurs if the solution will be directed through a narrow ion exchange.

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 [27]

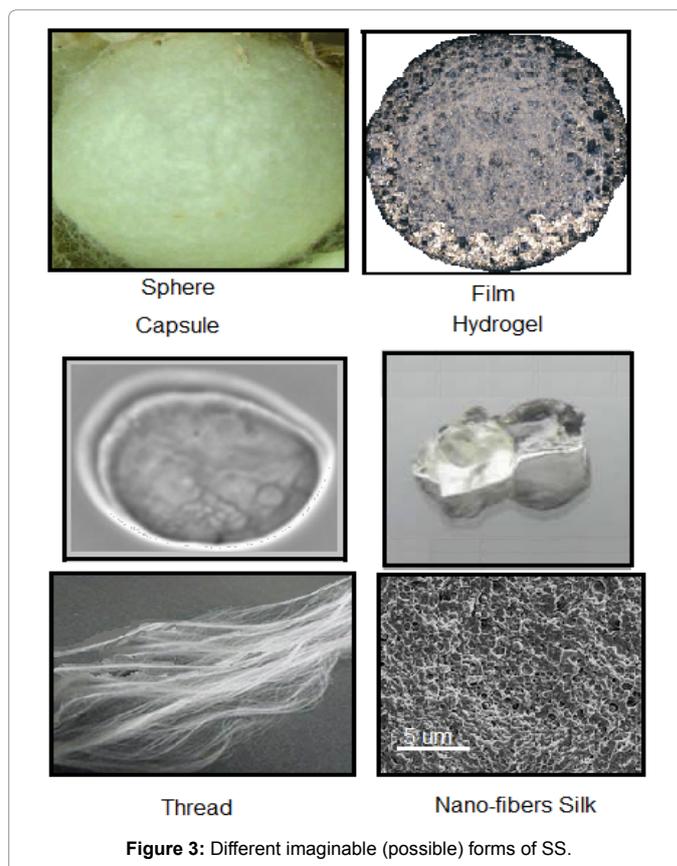
One can exceed nature when using SS in three dimensions. Figure 3 shows SS-protein with three dimension microscopic structures. Recently, scientists attempt to use SS-protein as biopolymer (novel biomaterial) for different applications. For example, researchers can prepare SS-films from a watered SS-sol [27]. 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  $\mu\text{m}$ '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 [27-30] 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 [27-30]. 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 [28-31]. 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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**Figure 3:** Different imaginable (possible) forms of SS.

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