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Spider silk: A natural marvel of mechanical and structural strength

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Abstract

The spider silk fibers have unique high performance properties that make it a desirable model for artificial fibers and its performance under benign conditions has important implications for biomimicry. It has tensile strengths comparable to steel and some are nearly as elastic as rubber on a weight to weight basis. The spider spins its silk at ambient temperatures, low pressures and with water as solvent. Spiders are ectotherms and the ambient temperature affects the spinning speed and the mechanical and structural properties of the silk spun. The high cytocompatibility and low immunogenicity of spider silk fibers make them well suited for biomaterial products such as nerve conduits. Spider silk proteins have been shown to be soluble in ionic liquids, thus once soluble, they can be processed into new biomaterials such as films, gels, porous sponges, bone tissue engineering. The spider silk chains with a fixed molecular weight decreases exponentially with the UV irradiation time, since UV irradiation causes the chemical bonds in the protein chains to undergo cleavage. This paper reviews related literature on the spider silk spinning process, conditions and their effects on structure, mechanical properties of spider silk and its resistance to UV degradation. As a bonus, a brief review of the biotechnological production of recombinant spider silk us presented.

Keywords: *Spider silk, Dragline, Spidroins, Microstructures, Recombinant, Mechanical strength*

1. Introduction

Spider silk has captured the interest of scientist for a long period, largely due to the unrivaled visual and functional properties of silk fiber and the unique structures that have been generated by various silk-producing species in nature. These structures include orb web structures spun to capture prey, cocoons to house offspring, adhesives used to anchor webs and fibrous tethers to capture flying prey (Kluge *et al.*, 2008). The silk fibers have unique high performance properties that make it a desirable model for artificial fibers and its performance under benign conditions has important implications for biomimicry (Agnarsson *et al.*, 2008). Spider silk is an outstanding fibrous biomaterial which consists almost entirely of large proteins (Heim *et al.*, 2009). Silk fibers have tensile strengths comparable to steel and some silks are nearly as elastic as rubber on a weight to weight basis (Yang *et al.*, 2005). In combining these two properties, silks reveal a toughness that is two to three times that of synthetic fibers like Nylon or Kevlar (Hinman and Lewis, 1992). Spider silk is also antimicrobial,

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hypoallergenic and completely biodegradable (Römer and Scheibel, 2008). It is regarded as one of the best natural polymer fibers especially in terms of low density, high tensile strength and high elongation until breaking (Lepore *et al.*, 2016) .

Spider silks are impressive biopolymers that have evolved over millions of years. Over the last several decades a lot of progress has been made in unraveling some of its secrets. Nevertheless, many questions, concerning production, solubility, storage aging and assembly of the underlying spider silk proteins, are still unanswered. The biotechnological production of recombinant spider silk in larger scales is a landmark in spider silk research, since now investigations are enabled to answer such questions. Furthermore, recombinant spider silk proteins can be processed into many different morphologies and shapes which have great potential in various technical and biomedical applications. With recombinant production technologies it is possible to create tailor-made silk-based biopolymers for many different purposes on a large scale within a relatively short amount of time..

2. Spider silk and the spider spinning process

2.1. Silk types

Silks differ widely in composition, structure and properties depending on the specific source (Altman *et al.*, 2003). Spiders produce silk from seven different glands with varying mechanical properties (Figure 1). The silk glands are found on the spinnerets, which are located on the spider's abdomen (Mariano-Martins *et al.*, 2020; Marples, 1967; and Mullen, 1969). The glands include the major and minor ampullate (used for locomotion and web frames), tubuliform (egg-case silk), flagelliform (capture spiral silk in orb-weaving spiders), aggregate (the glue in orb and cobwebs), pyriform (attachment disc for joining fibers) and aciform (prey wrapping silk) (Altman *et al.*, 2014).

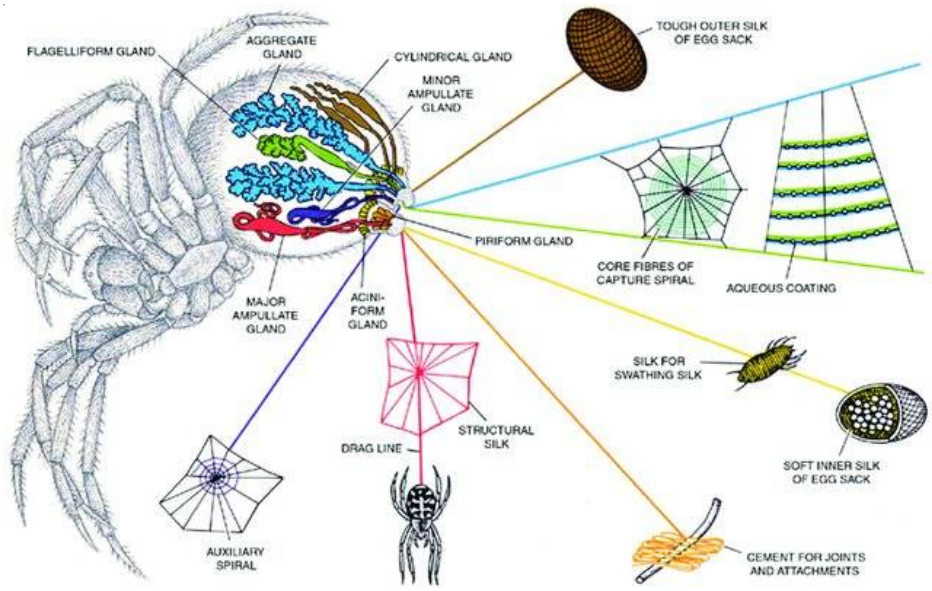

Figure 1: The seven types of native silk glands and threads from spider of *Araneus diadematus:* dragline/major ampullate silk (red), minor ampullate silk (purple), flagelliform silk (green), aggregate silk (blue), cylindriform silk (brown), aciniform silk (yellow), and pyriform silk (orange). The glands names are obtained from as mentioned in Vollrath (2000). Image reproduced from Zheng and Ling (2019)

The high extensibility of flagelliform silk are largely due to the interactions of its constituent protein molecules. The CDNA derived from this silk gland reveal that this silk is predominantly made from tandemly arrayed repeats of glycine-proline glycine (Blackedge and Hayashi, 2006a). An orb web consists of a framework of stiff and strong radial threads that supports a spiral of sticky capture silk, the primary means by which prey adhere to the web. The capture silk is highly extensible and covered with viscous glue, which allows the silk to gradually decelerate intercepted insects; thereby preventing prey from ricocheting out of webs (Shao and

Vollrath, 2002). The mechanical properties of the capture threads determine the length of time that an orb web can retain a captured prey (Blackledge, 2011).

2.2. Spider silk spinning process

Naturally, spiders like the *Araneus diadematus* store ADF-3 and ADF-4 proteins (MWs > 200 kDa) as highly concentrated (up to 50 wt %) solutions in a sac called lumen (Vollrath and Knight, 2001; Hardy & Scheibel 2009). When desired, aggregation of the proteins is triggered by certain chemical and mechanical stimuli, and the proteins are assembled into fibers. Taking the example of the dragline silk that has high strength characteristic, we look at the structure of the ampullate gland that secretes it. The ampullate gland consists of four parts as shown in Figure 2.

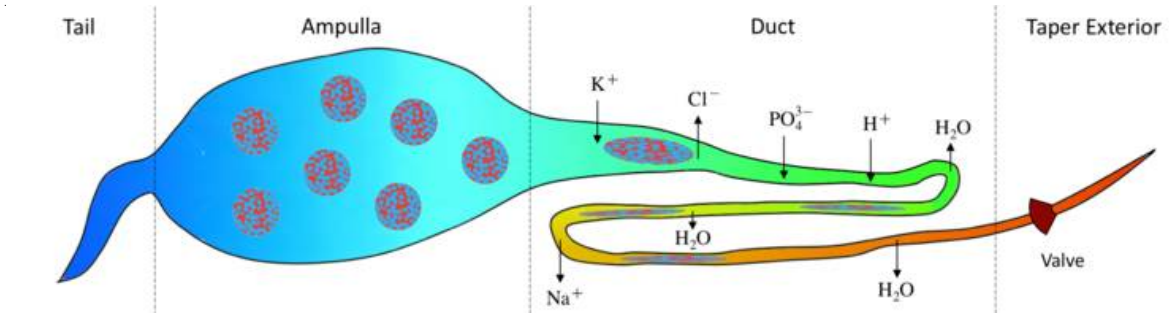

Figure 2: Structural hierarchy of the spider spinning apparatus. There are four major parts that are the tail, ampullate, duct and taper exterior (obtained and modified from Zhao *et al.*, 2019)

The primary proteins mentioned, which forms the primary structure are secreted first from the secretory granules in the tail (Vollrath and Knight, 2001). In the ampullate the concentration of the proteins rises and they form soft micelle of several nanometers aided by the neutral environment (pH = 7) of the ampullate (Kluge *et al.*, 2008). A mechanism driven by a mechanical frictional force squeezes the micelles into the duct and causes partial orientation by giving a long axis orientation of the molecules parallel aligned to the duct (Lefevre *et al.*, 2008). Several processes that includes water removal, ion exchange, acidification (which changes the pH gradually from 7.5 in the tail to 5), shear elongation that leads to phase separation happens in the duct and the final product is a high concentration liquid of silk in crystalline state (Eisoldt *et al.*, 2012; and Knight and Vollrath, 1999). The acidification induces the dimerization of the N-termini, while the C-termini unfolds exposing the hydrophobic areas thus assisting in fiber assembly. Finally, the silk is spun from the taper exterior and is 'extruded' via finger-like spinnerets as seen under an electron microscope in Figure 3. Once outside the spider's body, the molecules become more stable helixes and β–sheets from the liquid crystal (Zheng and Ling, 2019).

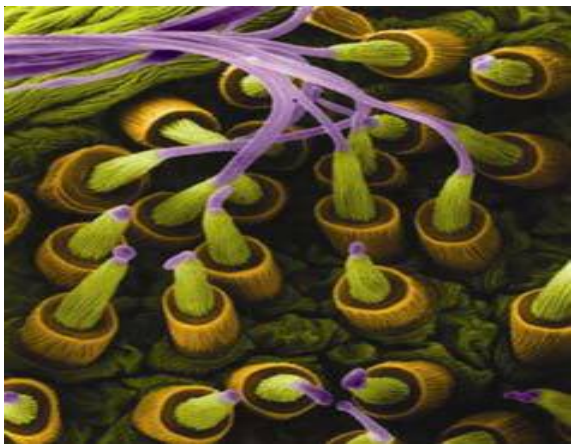

Figure 3: An electron microscope image of the finger-like spinnerets on the spiders' posterior abdomens used to extrude web silk (obtained from Das *et al.*, 2015).

2.3. Spider silk structure and protein folding

Spider silk is a fibrous biomaterial of the proteins referred to as fibroins. Its inner core is made up of a set of fibers called fibrils assembled though a process illustrated in §2.2 and further elaborated in Figure 4. Fibroins have repeated amino acids sequence motifs that form sticky crystalline structures embedded in an elastic matrix (Babb *et al.*, 2017; Chaw *et al.*, 2017; Correa-Garhwal *et al.*, 2019; and Yarger *et al.*, 2018). Other repeated motifs form amorphous spring like regions that allow extensibility (Swanson *et al.*, 2006). These motifs explain the high extensibility and low stiffness of the spider silk (Hinman and Lewis, 1992). The silk is a natural polymer that consists of a monomer of three domains: a repetitive middle core domain that dominates the protein chain and non repetitive N terminal and C-terminal domains (Tokareva *et al.*, 2013).

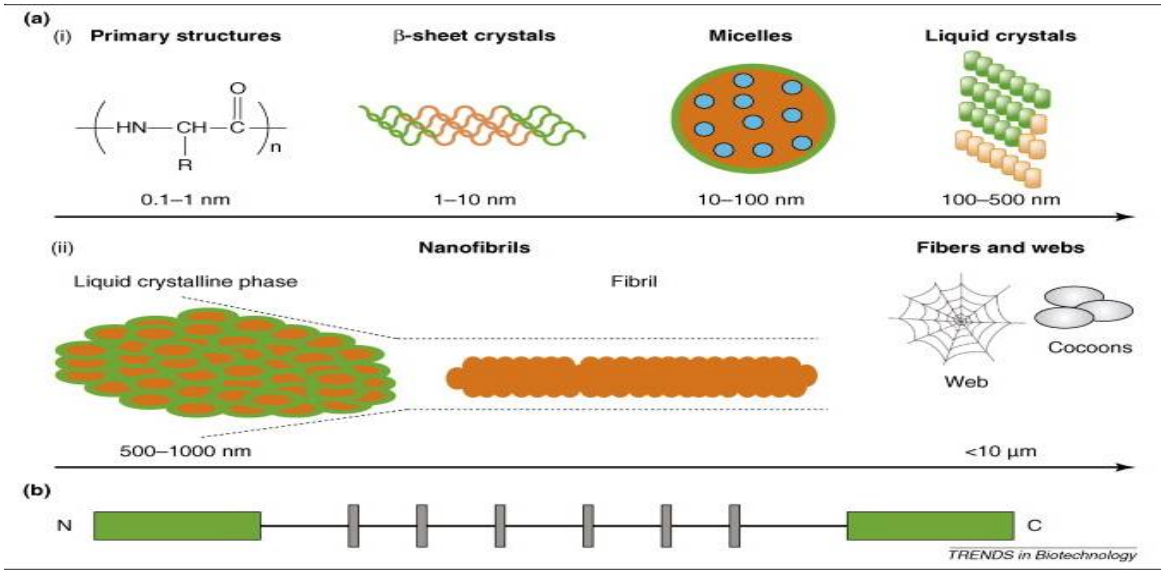

Figure 4: Structural hierarchy in silk assembly related to assembly into fibers. (a) (i) Repeat amino acid sequences ensemble into β-sheets. The β-sheet joins together soft micelles. As the protein concentration increases, micelles transform into gel-like crystalline structures; and (ii) Due to environmental factors, the gel state converts into a more stable β-sheet. The resulting fibrils are extruded as spider silk (Kluge *et al.*, 2008).

Silk produced by major ambulate (MA) is known as dragline silk. It is used by the spider to build the dry frame threads of their webs and also as lifelines when dropping from high places. It can match steel in strength but is also highly elastic and thus outperforms the best synthetic fibers in terms of toughness (Agnarsson *et al.*, 2008). It has a combination of elasticity along with a high tensile strength and toughness making it one of the toughest biomaterials (Shao and Vollrath 2002). It is about one-tenth the diameter of human hair (Frank *et al.*, 2001). It forms the cobweb's frame threads and is believed to be a composite of two different; spidroins designated as Masp 1 and 2 (Sponner *et al.*, 2005). The strength of dragline comes from the crystalline lattice that composes roughly 10% of the total webbing while its elasticity is as result of the amorphous region (Benmore *et al.*, 2012).

The spidroins have a high molecular weight, 200 to 350 kDa or even larger, are covalently linked via cysteine bridges in their termini and undergo further oligomerization due to their repetitive regions (Humenik *et al.*, 2011). These proteins contain alanine-rich motifs that form crystalline regions (Hinman and Lewis, 1992). They contain ordered crystalline and disordered noncrystalline regions (amorphous region). The crystalline regions contain stacked pleated β-sheets, whereas the amorphous region arranges as a matrix of helices, β-turns or β-spirals, and other protein secondary structures depending on the amino acid composition (Blamires *et al.*, 2012). The hydrogen bonds are broken when a temperature of 198 degrees is reached. The molecular chains separate and become disordered to give the rubber state. In such a state, the crystalline part of the silk still exists and provides multivalent crosslinks (Elettro, 2015).

As aforementioned, formation of the complex thread from spidroins occurs in the lumen of the duct connected to the gland, the spidroins traveling through the gland and duct experience a monotonic decrease in pH from

7.2 to 6.3 (Dicko *et al.*, 2004). Spider silk fibroins can adopt different structural states at high protein concentrations. They are soluble within the spinning dope of the glands, but readily converted into insoluble polymers upon extrusion (Sponner *et al.*, 2005). Different silk glands express fibroins with different proportions of crystal-forming and amorphous sequence elements, imparting different tendencies for the formation of crystals in their silk fibers.

2.4. DNA sequence to structure

The spidroins are modular, both sides of the long repetitive sequence has nonrepetitive amino- and carboxy-termini of approximately 100 amino acids. Major Ampullate spidroins are large proteins with an extension of 250-350 kDa, with an average of 3500 amino acids (Humenik *et al.*, 2011). They represent a polymeric organization, mostly based on highly homogenized tandem repeats. The stretches of alanine interrupted by glycine-rich repeats characterize the repetitive sequence. However, only 40% of poly-alanine sheets in silk fibers are highly ordered while the other 60% exist as poorly aligned sheet regions (Humenik *et al* 2011). The alanine and glycine-rich repeats in the repetitive sequence are not rigidly conserved (Xu and Lewis, 1990), see Figure 5.

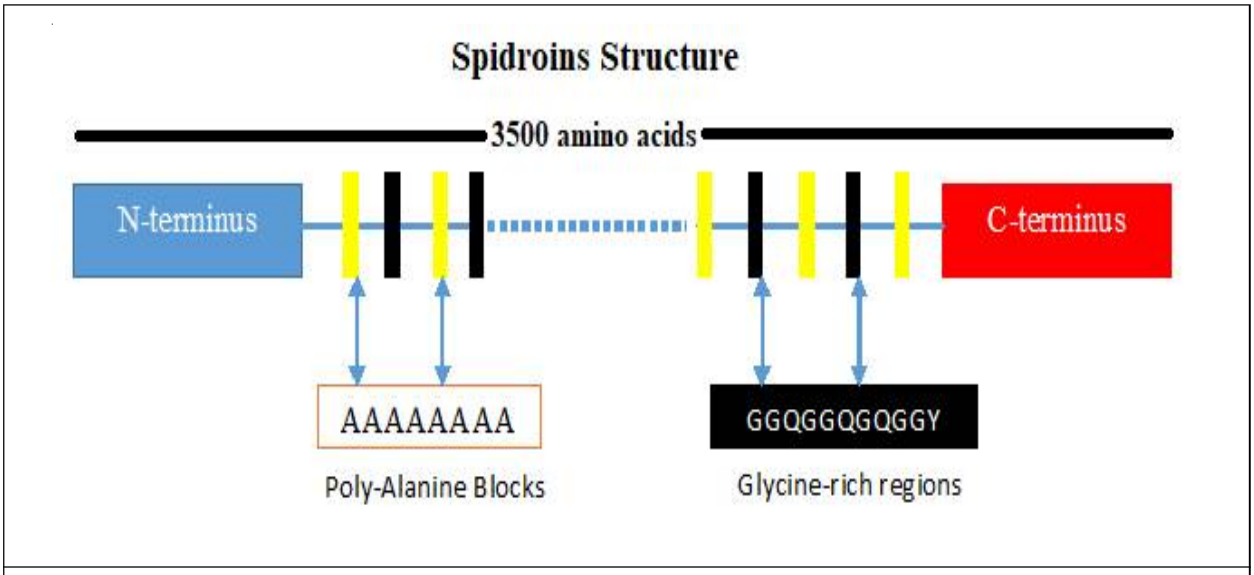

Figure 5: Structure of Ampullate spidroins showing interrupted Poly-Alanine and Glycine-rich regions

However, only 40% of poly-alanine sheets in silk fibers are highly ordered while the other 60% exist as poorly aligned sheet regions (Humenik *et al.*, 2011). Figure 6 shows the pattern of small crystal-forming blocks alternating with larger 'amorphous' blocks which is a feature of spider silk fibroins produced in at least three silk glands: the MA gland, the minor ampullate (MI) gland and the cylindrical (CY) gland (Gosline *et al.*, 1999).

The spider silk fiber consists of pseudocrystalline regions of antiparallel beta-sheet interspersed with elastic amorphous segments. The repetitive sequence of a fibroin protein form major ampullate silk of the spider (Van *et al.*, 2008).

MaSp1 and MaSp2 are large (about 250 to 350 kDa) and share general domain architecture (Sponner *et al.*, 2005; and Gaines *et al.*, 2008). They contain a large, central, repetitive domain that consists of about 100 tandem copies of a 30 to 40 amino acid repeat sequence. The repeat sequences for both spidroins are glycine-rich and end in poly-alanine motifs (usually four to seven residues long). For MaSp1, the consensus repeat includes $(GGX)_n$ (where X = A, L, Q, or Y) motifs and very low proline content. Contrary, the MaSp2 consensus repeat has significant proline content and characteristic motifs like GPG and QQ (Gatesy *et al.*, 2001). A relatively high level of amino acid sequence variation displayed by the repetitive domains of different spidroins provides the elasticity and toughness that is characteristic of the different fibers (Hayashi *et al.*, 1999). The repeat arrays of both MaSp1 and MaSp2 are flanked by non-repetitive N-terminal and C-terminal domains of approximately 150 and 100 amino acids, respectively (Xu and Lewis, 1990). The N-terminal and C-terminal domains found on mature spidroins are also conserved, among many silk types and spider species. These

domains play an important role for the functioning of the silk though they are relatively small in size. Both N- and C-terminal domains are rich in serine (~13% for N-terminal and 23% for C-terminal) and are predicted to exist as largely amphipathic α-helical secondary structures (Rising *et al.*, 2006).

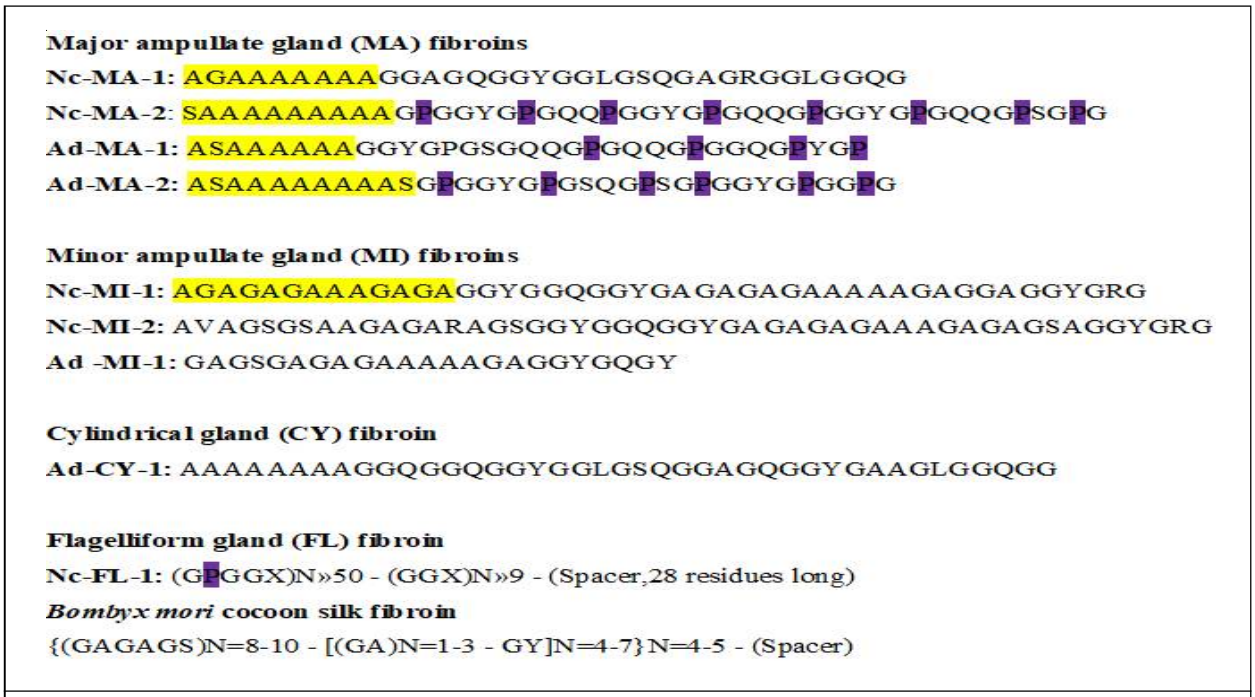

Figure 6: Amino acid sequence motifs for spider silk fibroins. Crystal forming motifs are highlighted in yellow; proline residues are highlighted in purple (Gosline *et al.*, 1999).

2.5. Silk spinning conditions

The mechanical properties of spider silk is affected by the 'extrusion' variables (Vollrath *et al.*, 2001) that includes; rate of spinning (Carmichael *et al.*, 1999; and Guess and Viney, 1998), spinning forces (Pérez-Rigueiro *et al.*, 2005), temperature during spinning (Yang *et al.*, 2005; and Glišoviæ and Salditt, 2007), post-extrusion treatment and other factors affecting the conformation transition of the spider silk proteins (spidroin) such as pH and metallic ions (Chen *et al.*, 2006; and Zhang and Tso, 2016). It is thus concluded that the spinning process plays a central role just like the spinning solution composition (Chen *et al.*, 2006). Since spiders are ectotherms, the highly variable environmental temperature is also the temperature of the fiber formation process and may range from 5-40 °C (Chen *et al.*, 2004). The ambient temperature affects the speed of movement hence affecting the spinning speed (Vollrath *et al.*, 2001). Silk reeling speed affects the diameter of silk thread. In web building the fiber is spun at approximately 1 cm s^{-1}, while when escaping predator, the rate is an order of magnitude faster. The different spinning rates do not result in identical microstructures, implying that the mechanical and structural properties should not be identical either (Guess *et al.*, 1997). The spinning speed also affects the breaking energy, stress and strain (Vollrath *et al.*, 2001).

Because the 'spinning dope' is liquid crystalline spiders can draw it during extrusion into a hardened fiber using minimal forces (Vollath *et al.*, 2001). Spiders possess a friction brake that allows them to control the tension applied to their silks when drawn, the forces exerted by the friction brake differ between natural and forced silking, i.e., when the force is high the fibers are stiffer than those naturally spun by spiders (Kojic *et al.*, 2006). Silk proteins flow through the gland as a concentrated aqueous solution, before being drawn from a spinneret. The proteins aggregate and form a fiber during the final stages of spinning. Many factors, such as the rate of drawing and other physiological factors, influence the chemical and physical properties of a given silk type (Koh *et al.*, 2015).

The silk is extruded via the spinnerets, which are located on the underside of a spider's abdomen, to the rear (Figure 3). The spinneret glands hold a liquid protein that crystallizes upon ejection. The cuticle that lines the gland's duct has the structure of an advanced hollow fiber dialysis membrane and facilitates a rapid removal of water and change in ionic composition involved in the spinning process (Vollath *et al.*, 1999). The

spiders control the properties of their major ampullate silk by applying shear force to silk as it emerges from their spinnerets. This shear force helps to determine the overall alignment of silk proteins, which are then ''frozen'' into place by hydrogen bonding and crystallizes to form the solid strands upon ejection (Blackedge *et al.*, 2012).

3. Recombinant spider silk proteins and potential uses

Substantial quantities of spider silk cannot be harvested from natural sources. Biotechnological production has been employed, thus providing recombinant spider silk proteins in more consistent quality and in larger quantities. Different host organisms such as bacteria (e.g., *Escherichia coli*) have been used to produce spider silk proteins, such as bacteria (e.g., *Escherichia coli*), since they portray fast growth kinetics, high cell density, and easy transformation (Rosano and Ceccarelli, 2014). In general the development of recombinant spider silk based biomaterials follows a scheme as shown in figure 7 (Selahi *et al.*, 2020). It begins with obtaining a 'blue print' from natural spiders DNA sequence, designing a recombinant DNA (factors to be considered include the morphology of choice, type of tissue to be engineered and its mechanical properties), vector cloning, selection of a suitable production host organism, e.g., bacteria, yeast, eukaryotic or insect cells, protein production through culturing and finally purification of the recombinant proteins. For example, MaSp2 spider silk proteins was produced at relatively high yields using *Escherichia coli* bacterial as a host based on the optimization of the genetic information of *Araneus diadematus* sequences (ADF3 and ADF4) (Salehi *et al.*, 2020).

In addition, recombinant produced spidroins allow introduction of nonspidroin functions by genetic manipulation, potentially enabling development of customized silk (Widhe *et al.*, 2012). Biotechnological spider silk production enabled genetic and chemical modifications to resemble the properties of the spider silk proteins (Humenik *et al.*, 2011). Functional peptides, such as the well-known RGD (arginine, glycine, and aspartic acid) motif from fibronectin have been incorporated to manipulate aminoacid sequence thus enhancing cell-silk interactions, or amino acids providing functional groups, e.g. cysteine residues with side groups for subsequent to modify the chemical of the silk protein (Aiqner *et al.*, 2018).

The mechanical properties of silk films are influenced by the content of β-sheet structure and crystallinity in the film. An Increase in the β-sheet structure of the film leads to an increased Young's modulus and strength, but lowers the elasticity (Humenik *et al.*, 2011). Silk films become stiffer and brittle as β-sheet regions increases and long-range order crystals (Spiess *et al.*, 2010). A mechanism of nucleation-aggregation, followed by concentration-dependent gelation can be used to produce spider silk hydrogels (Vepari and Kaplan 2007). These hydrogels can be combined with living cells to generate hierarchical tissue-like structures and used as an ink material in biofabrication (Jungst *et al.*, 2016). Spider silk porous films made of pNSR-16 and pNSR-32 (both containing RGD sequences) can be used to cover second-degree burn wounds (inflicted with 90 °C boiling water (Salehi *et al.*, 2020), through tissue engineering processes aimed at encouraging tissue regeneration, i.e., the renewal and regrowth of tissues (Selahi *et al.*, 2020).

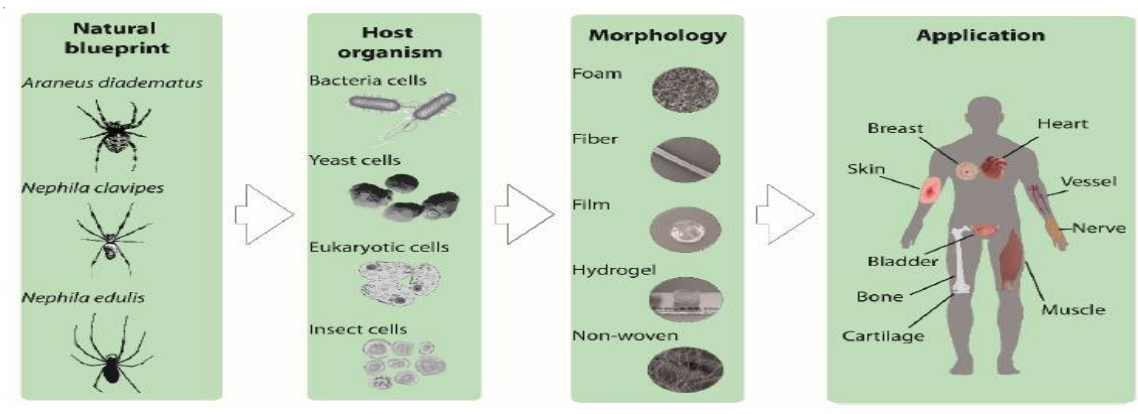

Figure 7: Schematic illustration or recombinant spider silk production. (1) A blue print is obtained from natural spider silk DNA, and a recombinant DNA designed. (2) Cloned vector constructs are transfected to host organism. (3) Different morphologies such as f oam, fiber, film, hydrogel, and non-woven mesh can be produced based to the target application. (4) Potential target application areas of recombinant biomaterials. Figure obtained and reproduced from Selahi *et al.* (2020).

4. Bio-applications of spider silk

Spider silk has extraordinary mechanical properties, is biocompatible and biodegradable, and therefore an ideal material for biomedical applications such as drug delivery systems and scaffolds for tissue engineering (Hermanson *et al.,* 2007; Agapov *et al.,* 2009; Gomes *et al.,* 2011; Allmeling *et al.,* 2013). However, it has not been commercialized for biomedical application due to its in homogeneity (Widhe *et al.,* 2012), as seen for other natural materials, as well as the low availability due to the cannibalism of most spiders (Schacht and Scheibel 2014). Silk fibers have proven to be effective in many clinical applications; however some biological responses to the protein have raised questions about biocompatibility. Sericin (glue-like proteins) causes adverse problems with biocompatibility and hypersensitivity to silk. If sericin is removed, the biological responses to the core fibroin fibers appear to be comparable to most other commonly used biomaterial (Altman *et al.,* 2003). By controlling material properties, spider silk can be used as drug carriers constant in plasma during therapy (Spiess *et al.,* 2010). Their high cytocompatibility and low immunogenicity of spider silk make them well suited for biomaterial products such as nerve conduits. Silk proteins slowly degrade enzymatically *in vivo*, thus allowing for an initial therapeutic effect such as in nerve scaffolding to facilitate endogenous repair processes, and then are removed (Radtke, 2016).

Ancient Greeks used cobwebs to stop wounds from bleeding and the Aborigines used silk as fishing lines for small fish. Silk was also used as the crosshairs in optical targeting devices such as guns and telescope. According to Harmer *et al.* (2011), 'spider silk's toughness and elasticity properties may be utilized in applications such as suspension bridge wires, bulletproof vests, and medical adhesives. By use of biomimicry spider silk proteins has been shown to be soluble in formic acid, HFIP, calcium nitrate, lithium salts and ionic liquids (Barr *et al.,* 2004; and Vepari and Kaplan, 2007). Thus once soluble, they can be then be processed into new biomaterials, including fibers, films, gels, porous sponges, bone tissue engineering (Melke *et al.,* 2016) and other related systems (Kluge *et al.,* 2008). Artificial spider silk, with mechanical and structural characteristics similar to those of native spider silk, can be produced from recombinant minispidroins and used in bone repair and regeneration (Yang *et al.,* 2010).

5. Mechanical strength of spiders silk

Spider silk has a unique combination of high storage modulus and high loss tangent that result in an immense capacity to dissipate kinetic energy (Work, 1985; Blackledge *et al.,* 2005a; Blackledge *et al.,* 2005b; Blackledge *and* Cherry 2006b, Gosline *et al.,* 1999). The high tensile strength comes from the poly alanine hydrophobic crystalline domains, while the links between crystalline domains as well as the elasticity of dragline fiber is from the glycine-rich regions that are hydrophilic (Xia *et al.,* 2010), see Figure 5. Studies have shown that the protein polypeptide chain network structure of spider dragline silks changes substantially with reeling speed. The β–crystallites exhibit a better alignment at higher reeling speed, implying that the protein macromolecules in amorphous state are better aligned under higher reeling speed and are more efficient in resisting external stress (Zhang and Tso 2016).

The resilience, elasticity, tensile strength and energy to break of spider silk is equivalent or superior to those of common metallic and non-metallic structural materials (Tarakanova and Markus, 2012). Major Ampullate (MA) silk has the most impressive mechanical properties of all spider silks, as it combines high strength with high extensibility (Hu *et al.,* 2006). Degradation processes that occur in silkworm silk and, in many polymers are also presents in spider silk. Ageing causes the cleavage of hydrogen bonds linking silk proteins, the decay of amino acids via emission of ammonia gas from the silk fiber and even oxidation (Blackedge *et al.,* 2012). Spider silk shrinks to half its original length and doubles in diameter when stored under water (super contraction). This is because hydrogen bonds are destroyed by water molecules; resulting in molecular chain motion and disorientation **(**Singha *et al.,* 2012).

The strength of the spider dragline silk can be enhanced by decreasing the size of the crystalline nodes in the polypeptide chain network while increasing the degree of orientation of the crystalline nodes. For dragline silk, the highest degree of orientation is almost reached at the natural reeling speed for spiders, and it remains as constant upon a further increase of the reeling speed, which leads directly to the stable mechanical performance of spider silk exhibited in nature (Du *et al.,* 2006). Spider silk has a better alignment of β–crystallites, a larger number of β–crystallites within the cross-section of a nano-fibril and a smaller effective loading area of a peptide chain which leads to stronger silk fibers. This explains the fact that the spider dragline silk fibers

having a lower crystallinity are much stronger than silkworm silk fibers (Xu *et al.,* 2014). Commercial silkworm silk is presumed to be much weaker and less extensible than spider's dragline silk. For example, Bombyx mori cocoons from silkworm has a tensile strength of about 0.5 (GPa), a breaking elongation of 15%, and a breaking energy (toughness) of 6×10^5 J/ kg compared to Nephila dragline silk, which has a strength of 1.3 GPa, a breaking elongation of 40%, and a toughness of 1.6×10^5 J/ kg. Table1 compares modulus, strength and energy to break of similar materials.

Table 1: Modulus strength and energy to break of similar materials (Tarakanova and Markus, 2012)

Material	Modulus (Nm^{-2})	Strength (Nm^{-2})	Energy to break (Jkg^{-1})
Spider frame silk	1×10^{10}	1×10^9	1×10^5
Kelvar	1×10^{11}	4×10^9	3×10^4
Cellulose fibers	3×10^{10}	8×10^8	9×10^3
High tensile steel	2×10^{11}	2×10^9	1×10^3
Tendon	1×10^9	1×10^8	5×10^3
Bone	2×10^{10}	2×10^8	3×10^3
Rubber	*ca*.10^6	1×10^8	8×10^4
Viscid silk	3×10^6	5×10^8	1×10^5

Force-drawn silkworm fibers compare favorably with Nephila dragline silk, silk spun at 4 mm/s (slow spinning) has a breaking elongation of (37%) for Bombyx silk while the breaking elongation for spider silk at the same speed is 35%. For faster spinning (13 mm/s) breaking energies are (1.2×10^5 J/kg and 1.6×10^5 J/kg) for Bombix silk and Nephila respectively (Shao and Vollath, 2002). Spider silk fibers can be braided into a bundle as in Figure 7, to improve its mechanical properties as shown in Table 2.

Figure 8: SEM of braided suture of 4660 single spider silk. Obtained from Hennecke *et al.* (2013). doi:10.1371/journal.pone.0061100.g001

Table 2: Tensile test results for spider silk sutures of 3 × 60 – 6 × 60, i.e., three, four, five and six bundles of silk with 60 single fibers (Hennecke *et al.*, 2013). doi:10.1371/journal.pone.0061100.t003

	3 × 60	4 × 60	5 × 60	6 × 60
n	12	9	10	4
Failure	2.99	2.37	2.49	2.52
SD	0.56	0.79	0.82	0.31

Table 2 (Cont.)				
	3 × 60	**4 × 60**	**5 × 60**	**6 × 60**
Failure strain (mm/mm)	0.55	0.53	0.48	0.47
SD	0.07	0.16	0.08	0.05
Failure stress (MPa)	581.0	316.5	266.8	226.6
SD	145	107.9	87.3	27.6
Modulus	2.01	1.30	1.04	0.62
SD	0.75	0.90	0.43	0.13

Different spider silk types produce distinct stress-strain curves, demonstrating that spiders spin a broad range of fibers with diverse mechanical properties. Spider silk fiber types have been studied using tensile testing and analyzed in Table 3 below.

Table 3: Mechanical properties of spider silks in comparison to other fibers (Hsia *et al.*, 2011)

Fiber	**Elongation (%)**	**Strength (GPa)**	**Energy to break (MJ/m³)**
Araneus dragline	27	1.1	160
L. hesperus dragline	34	1	nd
B. mori cocoon silk	18	0.6	150
Flagelliform	>200	1	150
Minor ampullate	30	0.346	nd
Tubuliform	71.7	0.629	nd
Aciniform	80	0.7	290
Nylon fiber	18	0.95	80
Kevlar 49 fiber	2.7	3.6	50
High-tensile steel	0.8	1.5	6

A study by Huang and Wang (2012), showed that a micrometer size dragline silk had an exceptionally high thermal conductivity up to 416 W m^{-1} K^{-1}, with the expectation that the thermal conductivity of the highly oriented antiparallel β-pleated sheets in silk fibrils be much higher. However, much intriguing was that the silk thermal conductivity increases with strain significantly, up to 19% increase at ~20% strain. This kind of thermal conductivity tuning could be highly valuable.

6. Resistance of spider silk to UV and seasonal changes

Ultraviolet (UV) radiations are energetic and most biomaterials are very weak when exposed to UV irradiation since it easily decomposes the protein molecules of natural silks such as silkworm silk (Becker and Tuross 1994; and Rus *et al.*, 2015). UV irradiation makes the chemical bonds in the protein chains to undergo cleavage (Sionkowska and Planecka, 2011). A chain of processes that leads to fragmentation of the proteinous silk ensues. The cleavage produces free ions that reacts with atmospheric oxygen to form radicals that induce the cleavage of other chemical bonds in the same chains as well as in other chains, thus amplifying the number of radicals (Pérez Rigueiro *et al*., 2007; Osaki *et al.*, 2004; and Koperska *et al.*, 2014). The high number of radicals further accelerate the cleavage of chemical bonds in the protein chains, thereby decomposing the spider silk chains into fragments with lower molecular weights (Osaki and Osaki, 2011).

Studies has found that silk and silk proteins from different spider species, diurnal or nocturnal spiders (Osaki and Osaki, 2011; Lai and Goh 2015, and Stellwagen *et al.,* 2016), and silkworm, behave differently under UV irradiation. For example *Nephila clavata* spider silk was found to be more resistant to UV irradiation compared to *Bombyx mori* silkworm (Osaki and Osaki, 2004). Comparing between spider and silkworms silk, it was found that the speed of degradation caused by UV irradiation was found to be 1.02×10^{-4} s^{-1} for spider silk and 1.75×10^{-4} s^{-1} for silkworm silk. This shows that the *N. clavata* spider dragline silk has a higher resistance to UV irradiation than silkworm silk. The difference in the UV resistance between spider silk and silkworm silk may be attributed to factors, such as the amino-acid sequence, β-sheet structure and molecular orientation (Matsuhira *et al.,* 2013). In order to preserve the mechanical function of the orb webs, some spider species have evolved from a nocturnal to a diurnal lifestyle in order to produce silk with sufficient UV resistance. This change was due to irradiation by sunlight (Osaki and Osaki, 2011).

7. Conclusion

In this review, spider silk fibers have been shown to have a sophisticated hierarchical structure composed of proteins with highly repetitive sequences. Their structure and extraordinary mechanical properties, defined by a unique combination of strength and extensibility, are superior to most man-made fibers has been outlined. To overcome challenges in harvesting in bulk silk form spiders and due to the aggressive territorial behavior of spiders, recombinant studies have been review. The ability to engineer silk proteins fibers has the advantage of tenability of properties too. The recombinant proteins can also be assembled into a variety of morphologies dependent on the target application. However, there is still much to learn from spider and silk spinning process. Further studies are needed that can make clinical trials of silk tissue engineering, and shed more light on the degradation of the natural and recombinant silk, in nature and application environments.

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