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Chapter 29

Applications of Silk

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Modern interest in silk started in the late 1960's with the first extensive mechanical property examination by Zemlin in 1968 *(1)*. Today, the same unique balance of material properties, good tensile strength, elasticity, and resistance to fracture is the primary driving mechanism behind the continuing interest in silks. Supercontraction, the mechanical response of some silks to moisture, has also been identified as being of potential technological value *(2-4)*. It is well known that the diverse primary and secondary structure of silk fibers is the basis from which some of their physical properties arise. Through interactions between and modifications of these structures to respond to specific chemical and mechanical environments, the spider tailors the properties of a particular silk for each specific application. It is this control of properties that we hope to better understand. Gosline stated it well in a recent interview *(5)*: "We do not aim to copy nature directly, but to adapt her designs and processes to our own purposes".

Using the spider's processing machinery directly to produce commercial silk is not viable. However, the possibility of using water-soluble precursors in a very energy efficient process that yields high performance fibers with controlled variability in their properties is an attractive goal. In addition, the final material could be environmentally friendly. This is in marked contrast to conventional fiber processes which typically employ environmentally undesirable solvents, (e.g. sulfuric acid for poly(para-phenyleneterephthalamide) [PPTA] and polyphosphoric acid for poly(para-phenylenebenzobisoxazole) [PBO]), require expensive precursors and large energy consumption and result in materials that are difficult to recycle/reuse. The potential cost savings from an industrial point of view is enormous. However, before such lofty goals can be achieved, we must first understand in some detail how nature utilizes the molecular control of chemical and physical chain properties to formulate protein polymers into materials with extraordinary mechanical properties *(6, 7)*. This chapter briefly summarizes applications for both fiber- and film-based silk materials. Most of the applications discussed take advantage of silk's unusual mechanical properties. Other more esoteric applications, including the use of silk gels as a cure for hangovers *(8)*, have also been proposed.

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Fiber-based Materials

Silk fibers have been primarily used in the textile industry due to their superior properties *(9)*. Starting in the 1800's in Madagascar, spider silk has been woven into a variety of clothing apparel including socks, shirts, ties, and dresses. The only other commercial use of spider silk fiber has been as reticle lines in optical devices *(10)*. Many uses for silk among native cultures have been documented including fishing lines and nets, as well as a number of sinister applications *(11)*. These include the dooming bag, a close knitted silk bag said to have a hypnotic effect, and the smothering cap, similar to a dunce's cap except made by matting spider silk, used for putting adulteresses to death.

Silkworm silk has been utilized for perhaps 6000 years, primarily as a textile fiber. An entire industry, sericulture, has been built upon raising, harvesting, and processing silkworms and their silk for this application. Silks are desirable for textile applications due to the mechanical properties and dyeability in addition to surface luster or sheen. In several museums examples are found of body armor from the times of Ghengis Khan, where leather and silk were used in combination to protect a warrior's body, especially from arrows *(12)*. The storied history of using silks in many ceremonial activities has also resulted in a need to understand how to best preserve these textiles *(13)*. Many "silk-like" synthetic fibers and textiles have also been produced in the past in order to provide lower cost facsimiles.

Recently, the excellent mechanical properties of spider silk fibers have led to a number of possible applications based on the property of large energy absorption before failure. This is a consequence of the fact that unlike most fibrous materials, silk elongation increases at faster loading rates. This gives rise to a number of shock absorber applications.

Research leading to these types of applications is ongoing in a number of laboratories as shown in this book. There is interest in using the fibers for personnel protection from ballistic projectiles *(14)*. From an orb-weaving spider's perspective, the sole purpose of the orb-silks is to absorb kinetic energy. To preclude web failure, the kinetic energy of the incoming prey must be dissipated. Through its viscoelastic response mechanism, the web dissipates 70% of this energy in the form of heat. The chemically harsh processing conditions necessary to process fibers currently used in body armor could be avoided if a silk-like material having similar or better properties were developed. The incorporation of high extensibility and high compressive strength silk fibers into lightweight cloth could have a significant effect on the way we design energy absorbing clothing.

The high tensile strength of silks would also be useful in the design of cables and ropes. This could be advantageous over conventional nylon rope in marine applications where high stretching ultimately leads to sudden and drastic failure. The high extensibility and the possibility of encoding saltwater protection into a silk-based fibrous material is one example. There is precedence in nature for this as several insects spin silks in an underwater environment *(15)*. These fibers possess their own unique set of properties. Cables or fish nets (even bungee cords) could potentially be made with superior properties if the costs were reasonable. The superior strength of lightweight fibers may also find use in the next generation of parachutes and high performance sails for sailboats and hang gliders. The ability to dye silk, already demonstrated by the conventional textile silk industry, is likewise advantageous.

The use of these materials in impact sensitive composite systems is also being considered for future applications *(16)*. Researchers hope that silk's potential high elasticity and tensile strengths will benefit applications requiring strong reinforcing fibers. The absence of kink-band formation, possibly an indication of good compressive strength *(17)*, could lead to applications where high compressive strength is required, such as structural components on vehicles with flexing wings or where impact damage from tools, ice, and stones is likely to occur *(16)*. Large recoverable deformations have been observed for both compression and extension for dragline silk from *Nephila clavipes*.

Since spiders produce a variety of silks, each tailored to a specific functional job, a wide range of additional applications may be realized when these other protein-based materials are understood. For example, adhesives which bond to a wide range of environmental substrates, even in wet conditions, and protective capsules derived from egg case silk are just two examples. Similarly, novel displays and responses in the electromagnetic spectrum *(18)* may prove useful in labeling, pattern recognition, and related scenarios.

The incorporation of silks into medical textiles is attractive because its protein-based molecular structure should yield excellent biocompatibility *in vivo*. Artificial tendons, blood vessels, and skin grafts could greatly benefit from the mechanical response of silks. Currently, silk fibroin is widely used as surgical thread due to its excellent mechanical and physical properties and good microbial resistance *(19)*.

Another potential benefit is the production of submicron diameter fibers which is in the realm of possibility using the spider's processing conditions. Man-made fibers of that size are difficult to make using conventional processes. These small diameter fibers possess superior properties, including high filament stiffness and strength*(20)*. which allows waterproof and windproof clothing that is permeable to water vapor to be manufactured. One could also speculate about applications such as corneal implants, where the submicron silk fibers would take the place of 30nm diameter collagen fibers *(21)*. The ability to control the molecular and microstructure will eventually lead to custom engineered mechanical properties.

Supercontraction of some silks has been postulated as having the possibility of doing molecular work. With the advent of micromachinery, one could conceive of a complex series of micromachines linked by ultra-fine spider silk fibers. The activation switch could be moisture causing a physical change in the amount of interaction through supercontraction. On this small scale, the high tensile strength would also undoubtedly be an added benefit. This phenomena could also possibly be utilized as moisture/humidity sensors.

Film/Membrane Applications

The complex secondary molecular structure of silks can be used to control specific interactions in different chemical and mechanical environments. The presence and amounts of particular secondary structure (silk I, silk II, α-helical, or random coil) of silk fibroin can be modified and controlled through stretching, compression, or with chemical and annealing treatments. These conformational changes can be utilized in the formation of membranes of stable, thin films for a variety of barrier applications*(22)*.

One area of current research interest is the use of silk in enzyme immobilization technology *(23-25)*. This approach can be used in the production of pharmaceuticals, cosmetics, specialty chemicals, fuels, and foodstuffs. Problems associated with immobilization of enzymes by conventional covalent coupling techniques can be reduced using silk-entrapped enzymatic systems. Advantages offered include the continuous operation of a microbial or enzymatic reactor, stabilization and higher activity of catalysts, and higher cell densities than those in conventional fermentation methods.

Although there are many different methods of immobilization available, their commercial applicability has been limited to date. Commercially produced chemicals using immobilization technology include the enzyme b-lactamase *(26)*, bulk chemicals ethylene oxide *(27)* and butadiol *(28)*, and the anti-inflammatory pharmaceutical shikonin *(29)*. Other promising applications include the immobilization of mammalian cells *(30)*, waste water treatment *(31-33)*, production and transformation of steroids *(34-36)*, and the production of antibodies *(37)*. To date, disadvantages encountered with proposed current immobilization methods include the mechanical instability of the support matrix, loss of enzymatic activity, harmful effects on the enzyme or cell due to harsh immobilization processes, and diffusional limitations.

Recently, researchers have examined a number of entrapment immobilization schemes to try to minimize these disadvantages. Gel systems such as calcium alginate and k-carraggenan have received the most attention due to successful ethanol production *(38)*. However, the main problem has been the weak mechanical stability of these systems, which leads to failure of the reactor systems due to increased pressure. Silk systems have recently shown promise as an immobilization matrix . A number of enzymes including peroxidase, glucose oxidase, and invertase have been immobilized successfully. One advantage of silk is the variability of its structure with slight changes in the environment. This allows the simultaneous insolubilization of the carrier and the immobilization of the enzyme without the use of chemicals. Tests indicate no disruption of enzyme activity, no inhibition to oxidation, good mechanical stability, and no diffusional problems in the incorporation of glucose oxidase for the development of a glucose sensor *(24)*. Biophotosensors have also been developed using an immobilized silk-based system *(25)*. The issue of embrittlement may be a factor if nonaqueous environments or ambient air exposures are encountered.

The degree of control which is available for silk systems leads to the possibility of their use in other permeable or semi-permeable membrane structures. Controlled delivery of drug dosages through capsules or membranes placed on the skin is one example. They could also be used as sensors for humidity or stress (especially compression). The large changes that the natural protein undergoes under a variety of environmental conditions may lead to devices where changes in this structure are used as a probe.

Conclusions

This paper has outlined a few of the potential technological uses for silk fiber and film technology. In this brief discussion we could not give proper attention to the long, difficult, and expensive research and development necessary to identify commercial applications or products for any new material. Indeed, just to list the properties that would have to be optimized for any successful application would significantly increase the length of this article. Therefore, this discourse only presents an abbreviated list of potential uses/products that current silk research could yield. In addition it is essential to recognize the need to achieve reasonable economic silk-production systems for these applications to be realized. This may occur through synthetic analogs, genetics with the native genes *(39)*, or genetics with synthetic genes *(40)*. Some of the most interesting applications for silk may in the long run not have anything to do with silk. For example, by developing a thorough understanding of the structure of the silk fibers we should be able to design new synthetic analogs tailored to achieve specific functional properties. Similarly, as we elucidate the processing steps and controls used in spinning silk fibers, an expanded field of environmentally-compatible approaches to fiber/film manufacturing may be realized.

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