

# WHAT MAKES SILK, SILK?

A guide to the science of silk and the opportunities for next-gen silk innovation

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#### Cover image: Haute couture fashion recently integrated Spiber's Brewed Protein™ next-gen silk yarns.

Source: Spiber, Inc. and Yuima Nakazato, Paris Fashion Week Spring Summer 2021 Haute Couture: https://www.spiber.inc/en/yuimanakazato/atlas/

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# INTRODUCTION

"Both scientists and fashion designers love silk, but until now there has been a disconnect between the scientific properties of silk and its desirable attributes as a fiber and fabric. In this report we connect the dots so that next-gen silk innovation, grounded in materials science, can meet the needs of the fashion industry and beyond." Sydney Gladman, Ph.D., Chief Scientific Officer,

Material Innovation Initiative

Often referred to as the "Queen of Fibers," silk is synonymous with luxury. Soft, smooth, supple, crisp, lustrous - for centuries, it has been difficult to match the unique properties of silk. Silk is one of our most ancient textile fibers, with the first silk fashion emerging in China around 2600 BCE.<sup>1</sup> Today, about 160,000 metric tons of silk are produced annually, primarily in China and India.<sup>2</sup> Commercial silk fabric is derived from the cocoons of silkworms via sericulture, the practice of farming silkworms. The growing silkworms are sacrificed for their precious cocoon fibers. As outlined below, recent concerns with environmental footprint and animal welfare have left many in the textile industry wondering why this ancient practice still exists in 2021, almost 5000 years since the first silk fabrics were introduced. That's quite a long reign for the Queen of Fibers. It's time for new leadership in the form of next-gen silk innovation.

But to dethrone the Queen we need to answer a few questions. What makes silk so special? How would one mimic or recreate silk without the harm of animals or the environment? In this report, we outline the science behind the composition, structure, and properties of silk that give rise to its unique performance. Further, we highlight the trends, challenges, and opportunities that exist in the next generation of animal-free silk materials.

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Look for the WS logo throughout this report for identified whitespace or untapped opportunities for next-gen silk innovation.

# ENVIRONMENTAL IMPACT OF SILK

According to the Higg Index developed by the Sustainable Apparel Coalition, silk has one of the highest combined cradle-to-gate Material Sustainability Index (MSI) scores, meaning it is considered one of the most environmentally damaging fibers.<sup>3</sup> Although the Higg Index does not tell the whole story of a material's environmental impact, it does showcase some of the key issues surrounding material production. Silk has a significant environmental footprint in terms of water scarcity and global warming potential. The farming of mulberry trees, which provide the sole food for silkworms, and the steps to transform the cocoon to the reeled fiber are very water intensive. It is estimated that between 850 and 1000 tons of water (equivalent to up to 20 average household pools!) are used in the production of one ton of

raw silk.<sup>4</sup> The use of fertilizer and manure for the support of mulberry production is responsible for the majority of the global warming potential of silk, alongside the drying of cocoons and fiber. According to one estimate, electricity consumption for cocoon drying is 1.0 kWh per kg cocoons<sup>5</sup> equivalent to 33 hours of binge watching on an LED TV.<sup>6</sup> Researchers in India report that 20 kg of firewood is consumed to generate 1 kg of raw silk.7 A life cycle assessment (LCA) conducted on raw silk produced in India reveals that silk has the highest environmental footprint across nearly all reported categories compared to cotton, nylon, or wool (Table 1).8 More information on the breakdown of process steps contributing to the referenced silk LCA can be found in Appendix I.

	Global warming potential (100 years; kg CO2 <sub>eq</sub> / kg)	Cumulative energy demand (renewable; MJ/ kg)	Cumulative energy demand (nonrenewable; MJ/kg)	Ecotoxicity (CTU <sub>e</sub> /kg)	Agricultural land occupation (m²a/kg)	Blue water footprint (m³/kg)	Freshwater eutrophication (g P <sub>eq</sub> /kg)
Raw silk (India)	51.5	1349.9	110.1	522.8	19.7	24.6	4.8
Cotton (China)	3.4	19.7	0.1	71.2	7.8	7	0.8
Nylon 66	8	1.3	0.0007	0.0006	0.0002	0.2	0.3
Sheep wool (US)	18.5	81.7	0.1	3.4	53.5	0.2	0.5

#### Table 1. Environmental impact of silk production compared with other fibers.8

Silk farming relies on approximately 300,000 households for its global production, and thus the social sustainability of silk farming is difficult to generalize.<sup>9</sup> While some tout silk production as a means to alleviate rural poverty, it is unclear if this is the reality for the fashion supply chain. Additionally, exploitation of child labor in silk fiber and fabric production has long been of concern in regions such as India and Uzbekistan.<sup>10</sup> Despite recent trends by specific silk suppliers to improve their sustainability via organic farming, fair trade approaches,<sup>11</sup> or the use of solar electricity,<sup>12</sup> the current reliance on animal agriculture still leads to environmental cost. The end of life for raw silk does not present as many environmental concerns due to its biodegradable and compostable nature.<sup>13</sup> Future reports from the Material Innovation Initiative will detail the environmental impact of animal-derived and next-gen silk.

The vast majority of commercial silk production relies on killing silkworms in order to harvest the silk cocoons. Between 420 billion to 1 trillion silkworms are killed annually to produce silk.<sup>14</sup> For more information on global production and animal welfare concerns regarding silkworm silk, see the Effective Altruism <u>Forum</u>.

The combination of high environmental footprint and animal welfare concerns leads to the question: can we make a new generation of silk that doesn't rely on animal agriculture, meets performance targets and improves upon sustainability? To do so, we need to understand "What Makes Silk, Silk?" Specifically, how does its composition, structure, properties, and performance make silk the luxurious fiber we know today? How can these be replicated and even improved upon? What are the historic and up-and-coming trends in silk alternatives?

# COMPOSITION AND STRUCTURE OF SILK PROTEIN FILAMENTS

In order to develop next-gen silk, researchers and innovators need to understand the fundamental science behind silk as it occurs in nature. As with all materials, the composition, structure, and processing of silk filaments are essential to their function. In this section, we outline the types of silk created by animals, the proteins that comprise these types, and the unique hierarchical structure of silk that informs its special properties. For innovators following bottom-up materials design principles (See **Current Strategies: Challenges and Opportunities**), this section gives introductory guidance on natural silk sequences and protein assembly.

#### SILK'S ANIMAL ORIGINS

Silk is a proteinaceous filament formed from the glandular secretions of animals such as insects, arachnids, and even sea creatures, for cocoons, prey capture, shelters/nests, wrapping mating "gifts," or securing eggs or their bodies to objects (see Table 2 for examples).

Two of the most studied silks come from the larval cocoons of silkworm moths, and the webs and other structures made by spiders. Silkworm silk is the most common origin of commercial silk

The spinnerets of a spider producing spider silk, imaged under a scanning electron microscope.

fiber and fabrics, and thus will be the focus of this report. Although silk fabric produced by spiders was never commercialized due to the difficulty in farming the cannibalistic spiders,<sup>15</sup> the unique engineering properties of spider silk have inspired many researchers and innovators to replicate its properties for fabric applications. Silk's unique properties have enabled applications in biomedical applications, electronic and optical devices, engineering composites, and many others, but in this report, we focus on the commercial application of silk fiber for fabrics in the fashion, home goods, and related industries.

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Sea silk is an ancient type derived from the byssus thread of mollusks. A rare sea silk hat was recently auctioned for \$14,400 by an investor.<sup>159</sup> Both these mollusks and this practice of sea silk manufacturing are nearing extinction. Could next-gen silk technology such as precision fermentation revive this unique form of silk, without the use of animals?



Image source: Edward Posnett, "Sea silk: the world's most exclusive textile is being auctioned this week," The Guardian, Nov 12, 2019. https://www.theguardian.com/fashion/2019/nov/12/seasilk-byssus-auction-textile-mollusks While other species have been identified for their production of silk, there are untapped opportunities to explore their application in commercial fabrics, or other applications in next-gen materials such as binders, resins, and coatings.



#### Table 2: Silk-producing animals and why they produce it.

Butterflies, moths (e.g., silkworm) Spinning cocoons<sup>16</sup>



#### Mayflies

For lining tunnels in submerged wood<sup>17</sup>



#### Spiders

Weaving webs to catch prey, protecting eggs, and producing safety lines<sup>18</sup>



Mollusks such as mussels Bonding self to rocks and surfaces<sup>19</sup>



#### Wasps

Binding with plant fibers to make nests or rope<sup>20</sup>



**Some crustaceans** Forming nests in sea kelp<sup>21</sup>



#### Dance flies

Wrapping paper for gifts during mating<sup>22</sup>



#### Figure 3. A simplified overview of silk processing.



Adapted from source: http://www.madehow.com/Volume-2/Silk.html

Cocoons from a number of silkworm species are used to make fibers and fabric of varying quality. For fabric applications, the silk derived from cocoons of the larvae of Bombyx mori (*B. mori*) moths, also known as Mulberry silk, is the most common commercially available type due to the ability to conduct large-scale cultivation and high throughput silk reeling, and thus will be the focus of this report. Absent additional context, assume for this report that "silk" refers to *B. mori* silk.

*B. mori* silk can be classified as bivoltine (harvested twice annually) or multivoltine (harvested throughout the year).<sup>23</sup> *B. mori* silk is is harvested from the cocoons of the larvae. In order to preserve

the continuous filament that forms the cocoon, the larvae are killed to prevent them from hatching and breaking open the cocoon.<sup>24</sup> The general process by which silk is processed from cocoon to yarn is shown in Figure 3. Other types of silkworms produce silk termed "wild silk" such as Tussah, Muga, and Eri silk. These silks are typically lower quality than the *B. mori* silk, because they have different protein compositions, naturally shorter filament lengths within the cocoon, and because the larvae are often allowed to hatch from their cocoons, further breaking the filaments. Due to their difference in composition and structure, wild silks also tend to be less fine and have less continuous length than *B. mori* silk.<sup>25</sup>

#### **PROTEIN COMPOSITION AND STRUCTURE OF SILK**

#### PROTEINS AND POLYMERS

Silk is formed primarily from protein. Proteins are naturally occurring polymers. (Polymers are the connection of many repeat units called "mers" or "monomers.") For proteins, the repeat units are amino acids assembled into a chain-like macromolecular structure. The sequences of amino acids are encoded by genes in the organism's DNA. Depending upon the composition and arrangement of these amino acid sequences, proteins have a variety of properties and conformations that control their function.

Polymers & Biology: DNA and RNA are polymers, (comprised of unique sequences of repeat units called nucleotides) used to encode and transport the instructions for assembling proteins such as fibroin in silk. This is often called the "central dogma" of molecular biology. A big part of biology is polymers that create other polymers!

Polymers, and proteins, can be amorphous or contain crystallites (semicrystalline). The former has limited order; the polymer chains arrange somewhat randomly, like a bowl of spaghetti. The latter form periodic tightly packed crystals interspersed in amorphous regions. Semicrystalline polymers often exhibit increased thermal and/or chemical resistance, and enhanced mechanical properties.



#### SILK FIBER STRUCTURE & COMPOSITION



Adapted from source: N.V. Padaki et al., "Advances in understanding the properties of silk," Advances in Silk Science and Technology (Elsevier Ltd., 2015): 7.

Upon extrusion from the silkworm gland, the raw silk fiber is termed a "bave." Two distinct regions comprised of the protein fibroin called "brins" are surrounded by the gummy shell of the protein seracin (Figure 4).<sup>26</sup> Silk fibers are processed to remove the majority of the seracin (and other sticky protein substances) from the filament, so that the main protein of silk is fibroin. Fibroin contains primarily glycine (H-) and alanine (CH3-) amino acids, which are among the simplest forms of amino acids, without bulky side groups. Although the fibroin structure actually contains three domains (the H-chain, L-chain, and P25 protein),<sup>27</sup> the primary structure of the silk fibroin protein (H-chain) is shown in Figure 5. Combined with a relative absence of interchain cross-links, this structure enables certain regions of the protein to fold into tightly packed crystalline structures.<sup>28</sup> The fibroin protein is based on a repeat of these crystalline segments, interspersed with amorphous The hierarchical nature of the silk fiber across length scales, from the smallest of amino acid sequences, to protein assembly and crystallization, to the formation of microfibrils, and finally up to the silk fiber, is critical to the unique mechanical properties of silk.

segments. In B. mori, the crystalline segment is much longer than the amorphous segment. The total length of the repeat sequence is ~80-600 amino acids. The fibroin protein assembles into aligned nanostructures which then form microfibrils via supramolecular assembly (Figure 4, 6). Bundles of microfibrils form the larger fibroin filaments.<sup>29</sup> This supramolecular assembly is dominated by intermolecular interactions such as hydrogen bonding, entanglement of the long polypeptide chains, and hydrophobic interactions. The hierarchical nature of the silk fiber across length scales, from the smallest of amino acid sequences, to protein assembly and crystallization, to the formation of microfibrils, and finally up to the silk fiber, is critical to the unique mechanical properties of silk.30



Because of these blocks of repeat units, silk protein is sometimes considered analogous to a type of synthetic polymer called copolymers. Copolymers contain domains of different monomers within the same long polymer chain. Copolymers can have unique properties compared to their homopolymer (or single type of monomer) counterparts. Because of this structural similarity, academic research has investigated novel copolymer compositions which mimic silk's structure (discussed in **Bottom-up Materials Design**). The protein component of spider silk, comparable to the fibroin of silkworm silk, is often called spidroin. The composition of the spidroin protein varies by spider species (~2500 spider species produce silk)<sup>31</sup> and can be more complex than the silkworm fibroin. Unlike silkworms, spiders produce silk for a variety of purposes, and can tune the properties depending upon the application by secreting the silk from different glands (see Mechanical Properties).<sup>32</sup> Spidroin differs from silkworm fibroin in that its primary repeat sequence is much shorter - only ~30-45 amino acids long. Its crystalline repeat structure is much longer than its amorphous repeat unit, whereas the opposite is true for fibroin (Figure 6). The percent crystallinity varies between species: B mori is thought to be approximately 50% crystalline, while Nephila spider dragline silk is 11-15%.33

In part because of this difference in protein composition, the properties of spider silk far exceed the properties of silkworm silk. This compositional difference is likely because of their respective evolutionary pathways: spiders evolved to make strong, tough fibers for web forming, where the fiber is the final form, while silkworms evolved to make protective composites to form cocoons. The fiber is the intermediate form to achieve the final structure.<sup>34</sup> The unique mechanical properties of silkworm and spider silk are discussed in **Mechanical Properties** below.

#### STRUCTURAL ASSEMBLY

The structure of silk is dependent on a balance of solution stabilization within the glands of the animal, followed by the on-demand assembly of the fiber. This balance is critical to converting the raw silk protein to the final fiber form. Generally speaking, the protein solution or "dope" within



Source: Amrita Sarkar et al., "Chemical Synthesis of Silk-Mimetic Polymers," Materials 12, 4086 (2019): 5.

the animal gland is theoretically characterized as comprising either micelles or liquid crystals.<sup>35</sup> Micelles involve the assembly of certain molecules in water, where hydrophobic tails become surrounded by hydrophilic ends. This is how soaps and detergents work to wash away oils and dirt. Liquid crystals behave somewhat like a liquid and somewhat like a crystalline solid. They are usually characterized by the spatial alignment of structures termed mesogens. By forming this micelle and/ or liquid crystal arrangement, the spinning dope stabilizes the proteins and prevents aggregation that would clog or solidify the silk within the animal gland.<sup>36</sup> Fine control over pH, ionic composition, and water content is also critical to stabilizing the dope. As the dope flows through the narrow ducts towards the spinneret, pH decreases and cations concentrations increase, and the solidification of the silk filament begins (Figure 7).<sup>37</sup> In addition, the shear and elongational forces during flow through the ducts align the protein molecules and promote their assembly into crystalline structures.<sup>38</sup>



Researchers are still uncovering nuances of silk protein assembly, and this fundamental science will be important for future attempts at silk replication.<sup>39</sup>

Figure 7. Schematic illustration of the programmed self-assembly of natural silk fibroin (NSF) driven by pH gradient and metal ions in the silk gland of the silkworm. There are a series of physical and chemical changes as the dope moves from the posterior silk gland (PSG) to the middle silk gland (MSG) and finally the anterior silk gland (ASG).



Source: https://www.biorxiv.org/content/10.1101/2021.03.08.434386v1.full

For *B. mori* silk, the seracin coating is thought to assist with water removal to dry the filament.<sup>40</sup> The delicate stability and solubility of the silk protein in solution, as well as the complex chemical and morphological changes necessary to achieve the structure of the silk protein and composite filament, are in practice quite difficult to replicate in synthetic silk. Artificially spun silks thus lack the robust mechanical properties of animal-spun silk.<sup>41</sup> Both silkworm silk and spider silk rely on the formation of extended beta( $\beta$ )-sheet crystallites, and are thus termed "canonical" silks. These beta sheets give rise to many of the interesting mechanical properties of silk fiber. Silks from insects and other animals that are "non-canonical" form crystal structures such as coiled-coils, helices, or cross- $\beta$  sheets.<sup>42</sup> Interestingly, researchers have discovered that non-canonical silk does not require

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Innovators could explore the production and properties of this untapped space of non-canonical silk to overcome some of the hurdles with the assembly of biomanufactured silkworm or spider silk. a secondary structural transition like the folding and crystallization of the  $\beta$  sheets.<sup>43</sup> Instead, the as-produced protein self-assembles into essentially its final form, and thus complex transformation in the spinning duct is not necessary. There has been less exploration of commercial silk fiber inspired by or composed of non-canonical silk. However, due to the relatively short amino acid sequences needed to form non-canonical silk protein, it is possible to produce high yields of recombinant protein by organisms such as *E. coli*.<sup>44</sup>

As described above, one of the critical aspects in the formation of the silk fiber from animal glands is the transformation of the dope (aqueous solution of silk protein) to extruded solid fiber. Interestingly, researchers have identified that the speed at which the dope moves through the spinning duct is a critical parameter for forming the crystallization and fibrillation inherent in the unique structure and properties of the silk fiber.<sup>45</sup> This process requires significantly less energy than inducing that same crystallization, alignment, and fibrillation in traditional synthetic polymers such as high density polyethylene. These learnings may enable next-gen silk innovators to refine the processing of wet spun silk to match the optimized flow conditions that occur in the natural spinning process.<sup>46</sup>



# FUNCTIONAL PROPERTIES OF SILK

The protein composition, assembly, and resultant hierarchical structure give rise to the unique dimensional, mechanical, thermal, electrical, optical, and environmental properties of animalderived silk.

#### DIMENSIONAL AND MECHANICAL PROPERTIES

#### **GEOMETRY AND DENSITY**

Generally speaking, textile fiber such as silk can be perceived at three length scales: the fiber, the yarn (i.e., a bundle of filaments), and the fabric (i.e., the manipulation of yarn into structures via knitting, weaving, etc.) (Figure 8). For naturally occurring fibers, the fiber properties are set by the biological origin and the processing needed to convert it to a workable fiber.

Figure 8: A schematic view of the three key length scales of fabrics: the fiber, the yarn, and the fabric.



Fibers are the raw material used to make textile items. They are spun or twisted together to make yarns.



Yarns are made from fiber from either natural or synthetic sources. They are interlaced, interlooped or bonded together to make fabrics.



Fabrics are made from yarns. Different fabric types are produced by different methods of joining the yarns together.

Silk fiber is unique. It is the only naturally occurring continuous filament fiber and it is smooth with low surface roughness (Figure 9). The continuous length of filament available in the cocoon, or the nonbreaking filament length (NBFL), is highest in the bivoltine *B. mori* silk at up to 800 meters (~2625 feet). Wild silks have much lower NBFLs ranging from 0.05 meters to 250 meters depending upon type.<sup>47</sup>

Most silk fabrics are created from reeled silk yarns made with a continuous smooth filament. A subset of silk fabrics can be made from yarn spun from shorter staple fibers of waste from the reeling process or fibers from lower quality cocoons.<sup>48</sup>

Fiber diameter can be difficult to measure particularly for fibers like silk with non-circular cross sections. Therefore, the textile industry employs other methods to compare the relative fineness of a fiber. Denier is a textile measurement of the linear density,<sup>49</sup> or grams per 9000 meters of fiber or yarn length. Interestingly, the denier system is derived from the standard of silk. Historically, one gram of silk fiber was approximately 9000 meters long, or one denier.<sup>50</sup> For a given fiber density, a smaller number means a finer fiber. An alternative unit is decitex, grams per 10,000 meters of fiber or yarn length. When silk filaments are combined into a yarn, the yarn count can specify both the fineness and the number of the filaments:

Silk is the only naturallyoccurring continuous filament fiber - up to 800 meters long - and it is smooth with low surface roughness. Figure 9. Microscopic appearance of various natural fibers. Note that silk has the finest diameter and smoothest structure of all of the fibers shown.



Source: https://www.nlm.nih.gov/ exhibition/visibleproofs/galleries/ exhibition/laboratory\_image\_13.html

Microscopical Appearance of Hairs from Various Sources, and Vegetable and other Fibers.
Figs. 22 to 35.—22, horse (back); 23, mouse; 24, cat; 25, chinchilla; 26, large hair from seal;
27, hair from head of female, age, eighteen; 28, hair from head of man after treatment with caustic soda; 29, fine hair from back of hand; 30, from head of child; 31, cross-sections of hairs from the head; 32, silk; 33, cotton; 34, flax; 35, wool.

# The diameter of a silk filament can be 10 times finer than a human hair.

e.g., 297 denier/150, indicates that there are 150 filaments in the yarn, and that each filament would be approximately 2 denier.<sup>51</sup> Fabrics can also be described by their areal densities or basis weight in units of gram per square meter (gsm). A unique areal density specific to silk is termed momme and is of Japanese origin. Momme is the weight in pounds of a piece of fabric sized 45 inches by 100 yards.<sup>52</sup> A higher momme is a higher "weight," meaning more tightly packed yarns and/or tighter weave structures in the fabric. A lightweight, sheer silk fabric like organza will have a lower weight than a denser fabric like charmeuse.<sup>53</sup>

The *B. mori* silk is the finest in the silkworm grouping, at 2-3 denier (~ 10-13 microns) for an individual filament.<sup>54</sup> For reference, the mid range value for the diameter of a human hair is ~100 microns, therefore a silk filament can be 10 times finer than a human hair!<sup>55</sup> Silk filaments are extracted directly from the cocoon, where reeling combines 8-10 ends of silk filaments from an individual cocoon into a yarn of specified count.<sup>56</sup>

The fineness of fibers is of critical importance for yarn formation, luster, and the handle and drape of fabrics. A finer fiber has a smaller diameter, which means its relative resistance to bending is decreased compared to larger fibers of the same type. This flexibility allows the silk filaments to have lower resistance to torsion (or twist) during yarn formation, which reduces its tendency to form snarls or kinks and provides a more uniform yarn.<sup>57</sup> The more uniform the yarn, the better the properties of the resultant fabric, including greater strength, extensibility, luster, fewer rates of



#### Figure 10. The differences in structure and morphology of silkworm silk (top) and spider silk (bottom)

Adapted from: Yan, Y. Advances in Technical Nonwovens. Chapter 2: Developments in fibers for technical nonwovens. (Elsevier Ltd., 2016). and John G. Hardy et al., "Polymeric materials based on silk proteins," Polymer 49 (Elsevier Ltd., 2008): 4311. breakage during textile processing, and a greater resistance to abrasion.<sup>58</sup> Fineness also makes silk fabrics more flexible with a more fluid drape.<sup>59</sup> Fabrics composed of finer fibers will also feel softer. With static touch, the minimum feature size a human hand can detect is 20 microns.<sup>60</sup> Individual silk filaments are smaller than this limit, and are generally featureless as well, which contributes to their soft hand. Wool, on the other hand, has larger fiber diameters and is known to give a "prickle" sensation.<sup>61</sup> (See Figure 9 for comparison of different natural fiber morphologies.)

Silk fiber has a unique triangular, nearly trilobal, cross-section (Figure 10, 11).<sup>62</sup> As described above, raw silk produced by the silkworm has two parallel fibroin-rich sections surrounded by seracin and a sticky protein coating (Figure 10).<sup>63</sup> The process of "degumming" removes the sticky protein and most of the seracin, leaving two triangular, prismatic fibers of fibroin (Figure 10). This triangular cross-sectional shape leads to interesting optical properties (see **Optical Properties**), but In order to replicate the unique comfort and aesthetics of silk, innovators should target next-gen silk to be formed into triangular, prismatic structures.



also contributes to the comfort of silk. Round cross-section fibers lie close to the skin and can be uncomfortable. The triangular form of silk has less available cross-section and leads to friction between the fabric and skin, which feels more comfortable or "crisp."<sup>64</sup>

Figure 11. Examples of the wide variety of fiber cross-sectional shapes possible with natural and synthetic fibers.



**Circular** Nylon, Polyester, Lyocell



Dogbone Acrylic, Spandex



Oval to round with scales Wool



**Triangular** Silk



Flat, oval, convoluted Cotton



**Trilobal** Specialty grades of nylon



Circular, serrated Rayon



Lobular Acetate

If recombinant silk fabrics are made with the round cross-sectional fiber like spider silk, they may have different characteristics compared to silkworm-derived silk, including notably different luster, friction, drape, and comfort. Unlike silkworm silk, spider silk is circular in crosssection, with multiple layers of varying composition (Figure 10).<sup>65</sup> Spider dragline silk is also incredibly fine, ~ 3-4 microns in diameter or 0.085 denier.<sup>66</sup> Fibers and fabrics made from recombinant silk protein are only now being developed (see more in **Current Innovators**).

#### **MECHANICAL PROPERTIES**

The mechanical properties of silk have attracted decades of interest by the academic community. Some important mechanical properties are described below and visualized on a simplified stress-strain curve (Figure 12):<sup>67</sup>

 Density: in units of mass per unit volume. Density is an inherent physical property related to composition and structure. While not a mechanical property, density is often used to normalize mechanical properties. When a mechanical property is divided by the density, the property is termed "specific" (e.g., specific strength, specific stiffness).

Figure 12: Simplified stress-strain curve showing the difference in mechanical properties between two materials. Material 1 (blue) has a higher strength and stiffness (modulus), but lower elongation at break and lower toughness than Material 2 (green).



# Silk is unique in that it is strong, tough, and moderately stiff and ductile.

- Elongation at Break: in units of percent. The maximum strain, calculated as the final length divided by the original length, that a material can incur before breaking. Sometimes referred to as the "stretch" or the extension of a material.
- Tensile Strength: in units of force divided by crosssectional area. The maximum stress a material can extend while being loaded lengthwise (i.e., stretching). For fibers, a similar value to tensile strength called tenacity, in units of gram per denier, can also be used.<sup>68</sup>
- Young's Modulus or Modulus of Elasticity: in units of force divided by cross-sectional area. The slope of the stress-strain curve, or the stiffness of a material (i.e., how much a material stretches under a given load).

• Toughness: in units of energy per volume. This is the energy required to break or crack a material and is often estimated as the area under the stress-strain curve.

Materials such as steel or carbon fiber tend to be strong and stiff, but brittle and they lack toughness. Materials such as rubber or wool can be ductile and tough, but not very strong or stiff. Silk, particularly spider silk, is unique in that it is strong, tough, and moderately stiff and ductile. Below is a summary of the key mechanical properties of silkworm and spider silk compared with other common materials.

Table 3: Mechanical properties of spider and silkworm silk compared to other common materials. Data sourced from Amrita Sarkar et al., "Chemical Synthesis of Silk-Mimetic Polymers," Materials 12, 4086 (2019): 1-24.

Material	Density (g/cm³)	Elongation at Break (%)	Tensile Strength (GPa)	Young's Modulus (GPa)	Toughness (MJ/ m <sup>3</sup> )
Dragline silk, A. diadematus	1.3	27	1.1	10	180
Flag silk, A. diadematus	1.3	270	0.5	0.003	150
Cocoon silk, <i>B. mori</i>	1.3	18	0.6	7	70
Steel	7.8	0.8	1.5	200	6
Elastin	1.3	15	0.002	0.001	2
Carbon Fiber	1.8	1.3	4	300	25
Kevlar 49	1.4	2.7	3.6	130	50
Nylon 6,6	1.1	18	0.95	5	80
Wool (at 100% relative humidity)	1.3	50	0.2	0.5	60

Figure 13. The specific strength and stiffness of natural fibers compared to those of the strongest man-made fibers. Several natural fibers such as silk are as good as, or better than steel.



Source: M.F. Ashby, The CES EduPack Database of Natural and Man-Made Materials (Granita Material Inspiration, 2008): 16

1e7 Elastic energy strorage Spider I he ability to store elastic energy per unit weight viscid silk Spider 1e6 drag-line silk (Tensile strength ^ 2)/ Young's modulus Sisal Silkworn silk Cotton an ski Keratin Human hai Wool Jute Ligament llemp Elm. Elastin Coir Cellulose Antler Pine, along grain Resilin Willow, along grain long grain Lignin Cortical bone Balsa, entine along g air Chitin Hydroxyapatit Cork Calcite Aragonite Bio-silica Abductin Coral 10 Balsa, Enamel Cancellous Lignum vitae, across grain 1 boneacross grain 100 1000 10000 Density (kg/m^3)

Figure 14. The maximum capacity to store elastic energy of natural materials versus density, showing how silk greatly exceeds the elastic energy storage capacity of all other natural materials.

Source: M.F. Ashby, The CES EduPack Database of Natural and Man-Made Materials (Granita Material Inspiration, 2008): 16

As shown in Table 3 and Figure 13 above, silk has a unique combination of stiffness (modulus), strength, toughness, elongation at break, and density. The specific strength of silk rivals or matches that of steel. Spider silk has by far the highest toughness of the compared materials, and even silkworm silk exceeds that of most materials. Interestingly, in this comparison, the material with the closest mechanical properties to silkworm silk is nylon 6,6. This explains why nylon stockings entered the market to replace silk (see **History of Synthetic Silk**). However, nylon does not have the same aesthetic properties as silk.

Another mechanical property similar to toughness is elastic energy storage. Compared to other natural materials, silk (both from silkworms and from spiders) has far and away the highest elastic energy storage capacity (Figure 14). Like a rubber band being stretched, silk acts as a spring and an impact absorber, holding on to a high amount of energy before breaking.<sup>69</sup>

### Innovators could explore tuning the draw rate of silk dopes in order to enhance the mechanical properties of the silk fiber.

Figure 15 shows the variety of silk outputs possible by the Nephila golden silk spider, ranging from high strength and stiffness in the major ampullate silk (used in the dragline or structural slk of the webs), to the stretchy, but low strength and stiffness of the flagelliform silk (used in the capture spiral of the web and as web coatings). The latter stretches over 3000% of its original length while wet!<sup>70</sup> Spider silk is an elastomer, i.e., a polymer capable of significant elongation or extension with rubbery characteristics.

Interestingly, silkworm silk can begin to match the mechanics of spider silk when forcibly reeled at different rates from the silkworm.<sup>71</sup> While forcibly

Figure 15: The spider has the ability to tune the mechanical properties of silk for a variety of intended purposes.



Source: Fritz Vollrath and David Porter, "Spider silk as archetypal protein elastomer," Soft Matter 2 (2006): 379.

reeling silk from silkworms presents a new set of animal welfare issues with silk production, this observation could be applied to synthetic silk preparation.

As discussed in **Silk Fiber Structure & Composition**, silk's hierarchical structure gives it these unique properties. Rigid crystalline segments in series with stretchy amorphous segments lend silk a tough protein structure. Alignment of these protein chains along the length of the fiber provides further enhancements in tensile strength and toughness.<sup>72</sup> In addition, the fibrillar nature of the silk fibers lends further toughness. If one fibril breaks, there are still many other fibrils available to shelter the mechanical load, and the breakage of each fibril requires energy.<sup>73</sup> The fibrillar structure of silk is not always a positive characteristic. This type of structure has weak interfibrillar bonds, which means that rubbing, abrasion, or even machine washing can break these weak bonds and lead to fibrillation and breakdown of the fiber.<sup>74</sup> See Figure 16 for an example of the damage that silk fabrics can incur after 15 wash cycles.

Researchers have attempted to replicate the structure and properties of silk in order to make new classes of engineering materials with similar mechanical properties. For fabric applications, these impressive mechanical properties enable the very fine fibers of silk to be robust enough to process from raw fiber, to yarn, to fabrics.

### The weak interfibrillar bonds of silk mean that rubbing, abrasion, or even machine washing can break these weak bonds and lead to fiber damage.

Figure 16. Left: unwashed silk fabric, middle: silk fabric washed with ultrasonic energy, right: silk fabric washed with washing machine for 15 cycles, noting fibrillation damage.



Source: M. Ma et al., "Effects of ultrasonic laundering on the properties of silk," Textile Research Journal 84 (2014): 2166.

#### THERMAL AND ELECTRICAL PROPERTIES

#### THERMAL PROPERTIES

Silk is a good insulator of heat compared to other textile fibers. With a specific heat of 1.38 J/gK, silk is similar, if not better, than wool or cotton when dry.<sup>75</sup> Silk also has one of the lowest thermal conductivity) values of textile fibers (Table 4). Thermal conductivity is the ability for a material to transfer heat through itself - where lower values indicate a lower propensity for heat flow. In other words, you lose less heat from your skin when wearing silk in cold weather, as the material prevents your body heat from escaping to the air.

Silk is stable under 100 °C, but will begin to yellow at ~110 °C after 15 minutes of exposure. Silk loses strength after exposure to elevated temperatures: 20 days at 100 °C results in 73% loss in strength, while 80 days leads to 39% reduction in strength.<sup>76</sup> Therefore, applying heat via ironing to silk fabrics must be done over short time scales and at low temperatures.

Silk's response to heat and water is used during the fabrication of silk yarn: steam heating allows for breaking of the intermolecular hydrogen bonds allowing the polypeptide chains of the silk to rearrange and align in the direction of the applied twist and tension in the yarn. Upon drying, the yarn is heat set as the hydrogen bonds reform.<sup>77</sup>

Table 4. Caption: Comparison of the thermal conductivity of silk compared to other natural and synthetic fibers.

Fiber <sup>78</sup>	Thermal Conductivity (mW/(m*K)
Air	25
Silk	50
Wool	54
Cotton	71
Polyester (PET)	140
Nylon	250

Silk's combination of low thermal conductivity and capacity to absorb moisture is what makes silk fiber comfortable in nearly all weather conditions. Silk's combination of low thermal conductivity and capacity to absorb moisture is what makes silk fiber comfortable in nearly all weather conditions.

Moisture absorption can remove perspiration to aid in comfort in warm weather. In hot, humid conditions, however, the low thermal conductivity and moisture regain can lead to lower comfort.<sup>79</sup> In cold weather, the low thermal conductivity of the silk keeps warm air closer to the skin, and when humid, the heat of sorption evolved upon moisture regain creates additional warmth (as explained in **Water** below).<sup>80</sup>

Unlike many synthetic textiles such as polyester, silk does not melt. Instead, at temperatures >250 °C in air, silk will char and decompose.<sup>82</sup> Silk, like other protein fibers, ignites with difficulty, burns slowly, and self-extinguishes. This gives silk some inherent flame resistance. Carbohydrate-based fibers such as cotton and linen, in contrast, ignite and spread quickly. The flame resistance of synthetic fabrics varies, but generally the fact that synthetics can melt once ignited makes them particularly damaging if they come in contact with skin.<sup>83</sup>

#### STATIC ELECTRICITY

Complex electrical properties of silk are important for advanced applications such as biomedical electronics, but for fabric applications, the ability to generate static electricity is most critical to performance. Fibers rubbing together or against surfaces can create a buildup of charges. If a fiber generates a lot of static, it can cause problems during textile processing and wearing, such as fibers sticking to equipment, attracting dirt or dust, or resisting folding. Static in fibers can result in garments sticking to one another or riding up while wearing. In extreme conditions, the discharge of static electricity can produce a spark that can start Figure 17: The effect of fiber cross-sectional shape on luster, showing the triangular structure of silk with the best degree of luster.



Adapted from: A.C. Cohen and I. Johnson, Fabric science. 9th edition (Fairchild Books, 2010).

a fire or explosion. Synthetic fibers suffer the worst problems with static buildup, proteinaceous fibers such as silk and wool have intermediate issues, and cellulosics the least.<sup>84</sup> Generally speaking, the more moisture in the air and thus in the silk fiber, the lower the potential for static due to dissipation of the static charges by water.<sup>85</sup>

#### **OPTICAL PROPERTIES**

The triangular, nearly trilobal shape of the silk fiber, its translucency, and its smooth surface lead to a high luster or the "shine" of silk.<sup>86</sup> Luster is a subjective property related to the reflection of light off a surface (Figure 17). Irregularly shaped fibers, such as cotton, will scatter light in many directions or absorb light, making them appear dull, or with low luster. More regularly shaped, smooth fibers will have greater luster. Packing of round fibers in a twisted yarn can cause light to be reflected in mostly the same direction, leading to strong or "harsh" luster. Triangular or trilobal shapes, similar to the silk fiber shape, allow reflected light to be concentrated in one or more directions associated with the three sides or lobes of the fiber. This concentration of light produces an almost "sparkling" effect.<sup>87</sup> In fact, synthetics such as nylon are designed with trilobal shapes for the purpose of enhancing sheen or luster in order to create fibers similar to silk.

As described above, silk filaments are also exceptionally fine. This fineness allows for a greater number of reflecting surfaces per unit area of the fiber.<sup>88</sup> This will "soften" the luster of the fabric to produce "sheen," whereas coarse lustrous fibers can have a "hard glitter."<sup>89</sup>

#### EFFECT OF ENVIRONMENTAL AND CHEMICAL EXPOSURE

#### WATER

Silk is hygroscopic and water can change its functional properties. Silk has a moisture regain of ~11% under typical conditions. The dry tenacity of silk fiber is typically 3-6 g/d (27-54 g/tex) and the wet tenacity is typically 2.5-5 g/d (23-45 g/tex).<sup>90</sup> Silk fibers swell about 30% of their volume in wet conditions. This swelling leads to lower dimensional stability compared to other fibers.<sup>91</sup>

Silk's moisture properties do have benefits, including comfort to the wearer in a variety of conditions. The hygroscopic nature of silk fibers means they uptake moisture such as perspiration from the skin, keeping the wearer comfortable in warm climates. Silk can absorb up to 30% of moisture from the air without feeling damp.<sup>92</sup>



# Innovators of next-gen silk would do well to use fiber shape to improve luster.<sup>93</sup>

Similar to other proteinaceous fibers such as wool, silk fibers have a moderate amount of heat of wetting/sorption (the amount of heat evolved per gram of water absorbed).94 When water is absorbed by the hygroscopic fiber, it undergoes an exothermic process of adsorption that releases heat. This means that the wearer has a greater amount of time to acclimate to cooler, humid weather conditions.95 This mechanism is most pronounced in wool, which is well known for its ability to keep you warm even in wet conditions. Synthetics that are hydrophobic, such as polyester, have very low heats of wetting and do not absorb much water. This is why wearing polyester can make you feel clammy or wet in similar weather conditions.96

Because the highly aligned, ordered microstructure of silk is held together with hydrogen bonding and is inherently metastable, water can disrupt this bonding and allow the silk structure to reorganize, which causes contraction and changes in properties.<sup>97</sup> Prolonged exposure to water, particularly steam or boiling water, will cause the peptide bonds which form the protein to hydrolyze, or break down.<sup>98</sup> This is part of the reason it is difficult to launder silk (fibrillation after washing shown in Figure 16).

In spider dragline silk, a unique phenomenon called supercontraction occurs upon immersion in water, with shrinkage approaching 50% in certain applications (Figure 18).<sup>99</sup> Redrying the silk results in loss of mechanical properties such as elongation at break or Young's modulus.

#### ACIDS AND BASES

Silk is relatively resistant to acids, but can be damaged in hot, concentrated acid solutions. In fact, weak acid treatment such as adding acetic acid (think vinegar!) to silk is one way to induce the "scroop effect," or the unique crisp sound resulting Figure 18: Caption: Supercontraction of spider silk from the major ampullate (MA) gland in water.



Source: J.M. Gosline et al., "The mechanical design of spider silks: from fibroin sequence to mechanical function," *The Journal of Experimental Biology* 202 (1999): 3300.

from rubbing certain silk fabrics together.<sup>100</sup> (See **What Makes Silk Special?**) During a weak acid treatment, a skin-like sheath of reoriented fibroin is formed around the fibers from the interaction with the weak acid, and this creates friction as the silk fabric is rubbed together. This same reoriented skin enhances the luster of the fiber as well, due to the increase in alignment of the fibroin chains on the surface.<sup>101</sup>

The acidic resistance of silk, coupled with its proteinaceous composition, make it particularly adept at dyeing with acid dyes, where the anionic (negatively charged) groups in the dyes bond with the cationic (positively charged) groups on the silk filament.<sup>102</sup>

In spider dragline silk, a unique phenomenon called supercontraction can lead to shrinkage up to 50% upon immersion in water.

# Exposure to sunlight or other forms of UV radiation will cause yellowing and degradation of the silk fibers.

Silk is most sensitive to alkaline (basic) or oxidizing solutions such as bleach.<sup>103</sup> Alkaline conditions will hydrolyze (or break the chemical bond of) the peptide chains, degrading the fiber, and reducing its luster.<sup>104</sup> Some soaps and detergents can be alkaline, which is another reason it is difficult to launder silk.

#### ENVIRONMENTAL

Silk is quite sensitive to ultraviolet (UV) light. Exposure to sunlight or other forms of UV radiation will cause yellowing and degradation of the silk fibers. The energy from the UV can cleave the peptide bonds within the protein chain and cause chemical reactions that alter the amino acid compositions and release ammonia gas.<sup>105</sup> In fabric testing, lightfastness is used to determine resistance to UV light (see **Silk Testing, Performance, and Grading** and **Appendix II. Example Performance Criteria for Silk Fabric**).

Silk is considered generally resistant to bacteria, fungi, and mildew in dry conditions, but this susceptibility is increased in humid conditions. Insects such as moths, silverfish, and carpet beetles are also known to attack silk fiber.<sup>106</sup>



# SILK TESTING, PERFORMANCE, AND GRADING

A variety of tests and standards apply to silk fabrics. Single-filament level testing, as described in previous section, is typically reserved for scientific investigations. Yarn or fabric-level testing is used in applied investigations for apparel or homegoods applications. Key organizations that create and manage these tests and standards are described below:

- American Association of Textile Chemists and Colorists (AATCC): <u>AATCC</u> is known for its standard methods of evaluating fibers and fabrics for a variety of performance characteristics including colorfastness, appearance, soil release, dimensional change, and water resistance.
- ASTM International (ASTM) and International Organization for Standardization (ISO): <u>ASTM</u> International was established in the U.S. to develop standards for measurement and testing of materials and assemblies. For fabrics, ASTM standards inform certain physical, mechanical, and chemical properties. ISO is an international organization of similar scope, but broader global participation, and includes ASTM as a member. There is significant collaboration between AATCC, ASTM, and ISO regarding standard development and guidance.
- U.S. Code of Federal Regulations (CFR): A subset of the <u>CFR</u> includes safety requirements by the Consumer Product Safety Commission (CPSC) for the manufacturing and use of consumer products. Of particular importance is the 16 CFR Part 1610, the code related to the flammability of fabrics.<sup>107</sup>

Third-party external testing services can perform tests, or they can be conducted in-house at mills, suppliers, or brands.

Below is a summary of some of the most important tests and standards that are typically applied to silk fabrics for meeting the performance requirements for specific fashion brands and retailers (Table 5). In general, most of these tests and standards apply to fabrics made from other natural or synthetic fibers. For some tests, there is a pass/fail or preferred minimum result For others, a preferred quantitative result may be required in a particular application. A survey of available standards for the fiber, textile, and apparel industry was published by NIST and can be viewed here: <u>link</u>. An example of the specific performance required by silk fabrics used at Nordstrom can be found here: <u>link</u>, and in **Appendix II**.

Because silk is a natural material, its quality can vary depending upon silkworm species, environment, and processing, or inherently from cocoon to cocoon. The International Silk Association has established a variety of raw silk grades ranging from 4A, 3A, 2A, A, and B, from highest to lowest quality. A Japanese method instead classifies silk from 5A, 4A, 3A, 2A, A, B, C, and D.<sup>108</sup> These classifications refer to the fineness of the raw silk (before degumming), degree of size variation (i.e., evenness), presence of imperfections (i.e., neatness, cleanness), tenacity or strength, elongation, winding ability, and other factors.<sup>109</sup>



Source: https://jamesdunloptextiles.com/journal/tips-how-to/2020-unraveling-textile-testing-abrasion-resistance in the second second

#### Table 5: Examples of common test methods specified for silk fabrics.

Test	Example Test Method <sup>110</sup>
Flammability	16 CFR Part 1610
Fabric Weight	ASTM D3776
Thread Count (warp/fill)	ASTM D3775
Yarn Size	ASTM D1059, ASTM D1244
Fiber Content	AATCC 20/20A
Dimensional Stability	AATCC 135/150, AATCC 158
Skew, Bowing	AATCC 179
Tensile Strength	ASTM D5034
Tear Strength	ASTM D1424
Seam Strength, Slippage	ASTM D1683
Stretch & Recovery	ASTM D3107, ASTM D6614
Abrasion Resistance	ASTM D4966
Pilling Resistance	ASTM D4970
Perspiration	AATCC 15
Crocking	AATCC 8/116
Colorfastness, Laundering or Dry Cleaning	AATCC 61, AATCC 132
Lightfastness	AATCC 16 E
рН	AATCC 81
Formaldehyde content	AATCC 112

# WHAT MAKES SILK SPECIAL?

Silk is often referred to as the "Queen" of fibers and fabrics.<sup>111</sup> Unlike many other natural textile fibers, silk is a continuous filament, with a smooth, lustrous appearance. Silk is the sole naturallyoccurring filament fiber; only synthetic fibers can be created in a continuous manner similar to silk (Figure 19, 21). All other natural fibers are staple fibers,<sup>112</sup> meaning that shorter length fibers are spun or twisted together to form a yarn (Figure 20). Yarn made from staple fibers are bound by aggregation or entanglement, and as such, individual fibers in the yarn may easily shed or pill under the shear forces of abrasion. For yarns made of non-biodegradable staple fibers, this means the yarn and end fabrics can produce microplastics more readily than a continuous filament yarn, which requires fragmentation of fibers for microplastics to be released. Silk is continuous, biodegradable, and not plastic, and thus does not contribute to microplastic pollution.



#### Figure 19. Categorization of various man-made (manufactured) and natural fibers.

Figure 20. Structural difference between staple fibers and yarns (top, e.g., cotton) and continuous filament fibers and yarns (bottom, e.g., silk)



The smooth, continuous filament gives silk yarn some of its unique properties such as lack of pilling, but also its strength and luster. As discussed in Silk Fiber Structure & Composition, the silk microstructure comprised of aligned crystallites within bundles of microfibrils imparts high strength and toughness at the single-fiber level. At the yarn level, these single fibers form the continuous filament yarn, which are more mechanically robust than an equivalent staple fiber yarn, due to the disconnected structure of the latter's single fibers.

Similarly, the tight packing of crystals in the silk microstructure, combined with the smooth, triangular prismatic surface of the filament, enables white light to reflect off the surface, making the fiber appear shiny or almost shimmering in certain angles. The high twist (or hard spun) silk will have greater luster than a low twist (or soft spun) silk, as the arrangement of the high twist enables more regular order. Generally speaking, the rougher the surface of a fiber (e.g., wool has scale-like structures that make the hairs rough), in combination with the degree of further roughness imparted by the disorder of staple fiber yarns, the less luster a yarn will have due to light scattering or absorption. The low roughness and high order of silk fiber and yarn contribute to its unique luster.<sup>113</sup> Silk is also known for its bright dyeability with acid dyes. The current generation of synthetic silks such as nylon and polyester often require disperse dyes, some of which have been associated with toxicity concerns.<sup>114</sup>

Figure 21. Silk is the only natural fiber that forms a smooth, continuous filament.



Source: https://mainetopmill.com/blogs/news/exploring-the-technical-side

Synthetics such as polyester lack the low conductivity and high heat of sorption of silk for cold weather comfort. Innovators should target these thermal properties.



Silk can have a waxy appearance from residual sericin coating, which results in frictional properties that contribute to its "hand" and sound. Rubbing some silk fabrics together gives a unique "crisp" sound sometimes termed wire-ming.<sup>115</sup> In French, this "swishing" sound of silk is called "scroop." This tactile feel and sound is important in the fashion community for identifying authentic silk. In fact, when fabric makers and designers evaluate imitation silk, they often prefer that it has a similar "scroop" to natural silk.<sup>116</sup> Figure 22 shows an article from 1907, noting that a cotton-derived imitation silk (likely rayon) "most closely resembles natural [silk,] its brilliancy being greater and its scroop slightly less."

Scroop is so integral to the silk experience that Japanese textile manufacturers use sound-wave tests on new fibers of imitation silk in an effort to match the susurrus of the real thing.<sup>117</sup>

Chemical treatments can increase silk's scroop, such as treatment with weak acids as described previously.<sup>118</sup> Some silk fabrics are made from fibers with reduced sericin content so that they are as smooth as possible. These silk fabrics are softer against the skin and have more "glissade" and less "scroop."<sup>119</sup>

This softness imparted by the smooth structure and small diameter of the silk fiber sets it apart from many other textile fibers. The fine, continuous nature of the fiber, combined with a lack of Figure 22. An excerpt from a 1907 newspaper article, profiling the earliest success of artificial silk - rayon.

Science threatens to put the silkworm out of business. French chemists have discovered at least 3 distinct methods of competing with the old reliable, but extremely deliberate silkworm.

Perhaps the most interesting of these is the manufacture of silk from guncotten, which also serves for a base for the most powerful of modern explosives.

The viscous fluid from which the silkworm spins its thread is chemically duplicated by a process described in the "Technical World." The fabric thus produced is inflammable and in order to remedy this defect it is treated with an alkale sulphide solution.

The founders of the new industry have kept in view not so much the exact reproduction of natural silk as the production of a substance which embraces its valuable properties.

Natural silk posesses to a large degree quantities of brilliancy, elasticity strength, affinity for colouring and bleaching materials, and when handled a peculiar rustling sound known as scroop. Perhaps the brilliancy and scrop of silk are the best known of its qualities, and it is in these two respectsthat antificial silk most closely resembles natural, its brilliancy being greater and its scroop slightly less.

Source: https://paperspast.natlib.govt.nz/newspapers/ GRA19070520.2.2 Figure 23. Images of Silk Chiffon, Silk Charmeuse (Satin), and Dupioni Silk. See Appendix III for microscopic analysis of silk fabrics.







The emotional element of silk as an "exotic luxury" item should not be dismissed. Madalyn Shaw, an expert in the history of silk, is quoted as saying: " A simple slip dress in satin can still make you feel like a million bucks; the same dress in linen makes you feel like you're dressed for the beach. It's not just tactile - there's an emotional response to it. It's the Orient, it comes from far away, it's mysterious--it has all that going for it."<sup>121</sup>

By combining different arrangements of filaments into types and sizes of yarns and weaving those yarns into varying patterns and densities, a variety of silk fabric types are possible with unique aesthetics and performance. For example, chiffon silk fabric has a low-density structure in order to be transparent, gauze-like, and delicate. Silk satin or charmeuse fabric has a front face with exquisite gloss and fluidity with a duller backing. Charmeuse, chiffon, georgette, and crepe are all considered to have a fluid drape.<sup>122</sup> One the other end of the spectrum, dupioni silk fabric is crisp and stiff, with voluminous drape,<sup>123</sup> and surface bumps and irregularities.<sup>124</sup> See Figure 23 for photographs of chiffon, charmeuse, and dupioni silk. There are many types of silk fabric, but all rely on the individual silk filaments to form them. Microscopic analysis of a variety of commercially available silk fabrics shows that although the same, smooth, continuous filaments are employed in all fabrics, brilliant dyes and unique yarn structures can result in wildly different aesthetics (Figure 24, see Appendix III for further microscopy of silk, polyester, and cotton fabrics). Differences in the processing of silk filaments to form the yarns and fabrics can also result in different aesthetics. For example, dupioni silk fiber is usually simultaneously reeled from two different silk cocoons (double cocoons nested together), which causes the characteristic bumps and irregularities.125

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A true silk mimic needs to retain the exotic, luxurious properties of natural silk in order to be successful.

By combining different arrangements of filaments into types and sizes of yarns and weaving those yarns into varying patterns and densities, a variety of silk fabric types are possible with unique aesthetics and performance.

Figure 24. Optical microscopy of various silk fabric swatches, taken at 200x magnification. Scale bar is 200 microns.







Silk Shantung

Silk 4-ply crepe

Silk charmeuse



Silk plain organza



Silk crepe de chine



Silk chiffon



Silk mesh tulle



Silk habotai or china silk



Silk double georgette

MII would like to thank the laboratory of Prof. Jennifer Lewis, Sc.D. at Harvard University for equipment access to obtain these images.

# THE DESIGN POSSIBILITIES OF SILK FABRIC

# PERSPECTIVES FROM THOMASINE DOLAN, FASHION DESIGN SPECIALIST, MATERIAL INNOVATION INITIATIVE.



Christian Dior at Couture Spring 2020 Source: ImaxTree



Ralph Lauren at New York Spring 2005 Source: ImaxTree



Ralph Lauren at Spring 2015 Source: Getty Images

#### CHRISTIAN DIOR SILK CHIFFON

"This fabric is very fine, sheer and light. And since chiffon is not as slippery to work with as silk charmeuse or satin (which is both heavy and slippery), this fabric can be fed into the tiniest of gathers for draping or sewing as illustrated above in this Christian Dior gown."

#### RALPH LAUREN SILK SATIN

"The super smooth, cool hand of satin feels immediately luxurious. Few fabrics catch the light like satin. Satin comes in a variety of weights and is often used for bridal gowns. It's slippery hand makes it difficult to sew, adding to the cost of the (already expensive fabric) finished garment because it requires a highly skilled person to drape, cut and sew this fabric. It's known for its fluid drape, shine and movement when walking."

#### RALPH LAUREN SILK TAFFETA

"You can practically hear this fabric walk just by looking at the photo. This is a fairly lightweight silk taffeta but still delivers on 'crunch sound' if you were to put a bunch of it in your hands and gently crush it. This may be the only silk material that when you rub two pieces of taffeta together creates a sound. There is a little bit of 'tooth' to this fabric. It is an extremely tight weave."



Salvatore Ferragamo at Milan Fashion Week Spring/Summer 2012 Source: Style.com & INFDaily

#### SALVATORE FERRAGAMO LIGHTWEIGHT SILK CHARMEUSE

"Nothing takes color as beautifully as silk. All silks were meant for walking you can see the way air fills the fabric creating a parachute effect. When cut generously these lightweight silks create dramatic volume. Like satin, silk charmeuse is slippery and, therefore, difficult to sew."



Available to purchase at Net-A-Porter.com

#### **OSCAR DE LA RENTA** SILK FAILLE

"This fabric has so much structure it can practically stand on its own if sewn into a cylinder shape or column, like this dress. Pleating creates a 'rounded' edge due to the strength of the weave. Faille gives a very low lustre/sheen because the surface is not totally flat. This fabric is often used in couture as it lends itself to dramatic silhouettes."

# HOW COULD SILK BE IMPROVED?



Silk has many positive attributes, but also a few drawbacks. Innovators and researchers could target negative attributes as a means to outperform animal-derived silk.

One of the biggest challenges with silk is one that all wearers have faced: don't get it wet! There are two reasons to avoid water with silk: 1) running or bleeding of certain water-based dyes, and 2) shrinkage, warping, or damage of the silk fabric.<sup>126</sup> Silk is hygroscopic, meaning it absorbs moisture, and can lose strength when wet, making it more susceptible to damage from creasing, dulling from fibrillation, or fabric deformation<sup>127</sup> The moisture absorption of silk can aid in comfort, but too much can lead to fabric damage.

Even more so than *B. mori* silk, spider silks are known to shrink substantially after exposure to water. Spider-silk mimicking material company, Spiber, noticed this issue in their early use of recombinant spider protein materials. Spiber redesigned their protein away from the natural spider protein in order to reduce shrinkage.<sup>128</sup> This is just one example of how custom-designed recombinant proteins could transform the properties of silk fibers.

As previously described, silk also has poor resistance to UV light. Exposure to UV sunlight can result in fading of the dyes or yellowing of white silk and can degrade the mechanical properties of the silk fiber. Silk has a lower long-term heat resistance than many other natural or synthetic fibers, which is why it is preferred to steam silk rather than directly apply a hot iron.

Despite the high strength of silk, the fine (i.e., small diameter) nature of the silk filaments and their use in thin fabrics can make them susceptible to damage from snags or wear. In particular, the weak bonding between microfibrils forces fibrillation, or fibril separation, to occur under abrasion forces, which weakens the fiber.<sup>129</sup>

Because of silk's incompatibility with water and heat and the fine nature of the fibers, traditional laundering is rarely an option for silk fabric. Normally, all silk fabrics must be dry cleaned. Alongside its relatively high cost compared with cotton or synthetics, silk is often reserved for luxury apparel and accessories such as scarves, that are rarely laundered and/or worn less frequently, in order to undergo less wear and tear that will degrade the fabric.

Silk's environmental impact, cost, and reliance on animals for production are notable negatives. With advancements in material and fiber science, we can create fibers that mimic the positive properties of silk, and improve upon its negatives. With continued innovation and technological advancement, we can replace silk with affordable, high-performing, sustainable alternatives.

Because of silk's incompatibility with water and heat and the fine nature of the fibers, traditional laundering is rarely an option for silk fabric.

# APPROACHES & CHALLENGES TO CREATING ANIMAL-FREE SILK

Innovators of next-gen silk need to know the current landscape of animal-free silk approaches and the opportunities and challenges that currently exist in next-gen silk innovation. In this section,we outline the history of synthetic silk, the current strategies for next-gen silk development, the unique market opportunities of silk, and the challenges associated with next-gen silk innovation.

#### HISTORY OF SYNTHETIC SILK

Some of the earliest innovations in synthetic fibers came about in an attempt to replace silk fiber. Invented at the turn of the 20th century, rayon (a form of regenerated cellulose) was the earliest form of artificial silk. In the 1930s and 40s, nylon entered as an alternative to silk stockings.<sup>130</sup> Nylon was actually a preferable material for this application to silk. Nylon stockings were more durable and easy to care for, and did not "run" as easily as their silk counterparts. This use led, of course, to the now colloquial term for stockings as "nylons." Nylon was adopted very quickly. Within two years of introduction, nylon from Dupont had captured a third of the hosiery market. During WWII, a black market for highly desirable nylon stockings was created when the United States military diverted use of nylon to military applications in parachutes and ropes.<sup>131</sup> A short time later, polyester fibers hit the scene as another silk-like fiber. In the 1970s, polyester suffered from the "double knit polyester" curse of perceived cheapness and discomfort. Recent textile innovations such as microbers, or fine diameter filaments, made possible by the versatility of this easy-to-process and durable polymer, have enabled polyester fabrics that are virtually indistinguishable from silk, cotton, or even wool.132 Today, these same synthetics are still common alternatives to silk and are even used to mimic the drape and

luster of fine silk fabrics.<sup>133</sup> Microfiber technology has enabled synthetics such as polyester to be made into fibers even finer than silk, giving way to uniquely soft, high drape fabrics.<sup>134</sup> However, many in the fashion industry feel that these materials fall short in aesthetics, performance, or sustainability. Some cellulosics have been called out for issues with deforestation and downstream effects of chemical processing, while nylon and polyester are petroleum-derived materials contributing to our current microplastic pollution crisis. Synthetics such as polyester are often known for poor comfort as the fibers are stiffer and less absorbent.<sup>135</sup>

#### CURRENT STRATEGIES: CHALLENGES AND OPPORTUNITIES

"New fibres came as a result of trying to create a replacement for silk. Now we have the possibility of a replacement that really is silk."

- John O'Brien, DuPont Central Research.

Source: J.E. Lydon, "Silk: the original liquid crystalline polymer," *Liquid Crystals Today* 13, 3 (2004):10.

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A white space of opportunity exists for biodiscovery to create a library of recombinant silks with unique properties. Did you know that animal-free silk produced via fermentation technology is already accessible to consumers in skin & hair care products? Innovators in recombinant silk protein synthesis might explore these markets in addition to textiles.<sup>136</sup>



Academic investigations to replace silk have been active for decades, but few sustainable alternatives to silk are currently at commercial scale. Generally speaking, the technologies come from two broad categories: bottom-up materials design and topdown materials design.

Both forms of materials design are biomimicry, i.e., attempts to emulate the function of a natural material.<sup>137</sup> For the bottom-up approach, innovators work to understand and to replicate the mechanisms behind the natural material that give rise to its unique function. For silk, the polymeric composition, assembly, and hierarchical structure of the fiber give rise to its performance. For the topdown approach, innovators tailor the manufacturing of synthetic or regenerated materials in order to mimic the properties of the natural material. An overview of the techniques, challenges, and opportunities for both of these categories is described below.

#### **BOTTOM-UP MATERIALS DESIGN**

Bottom-up design includes technologies that recreate the silk protein via cellular engineering approaches. Precision fermentation technology, for example, inserts silk protein genes<sup>138</sup> into microorganisms such as yeast and bacteria in order to produce recombinant silk protein, also termed heterologous proteins or foreign proteins.<sup>139</sup> Similar techniques can be employed with insect cells, animal cells, or plants to produce the target protein.<sup>140</sup> To date, precision fermentation has only been commercially approached for spider silk protein, rather than the more commercially available B. mori silk. There are three reasons for the focus on producing spider silk protein: 1) The lack of animalderived spider silk, due to the difficulties inherent in large scale farming and collection of silk from cannibalistic or aggressive spiders, makes spider silk protein an untapped market. 2) The engineering properties of spider silk surpass those of B. mori silk. 3) Spider silk is formed from a shorter repeat sequence of amino acids. It is easier to insert genes for smaller sequences than the larger repeat sequence of B. mori silk protein.

However, there is no reason that the current next-gen silk approach of recombinant protein synthesis be limited to spider silk spidroin or even to the fibroin of *B. mori.* As shown in Table 2, there are numerous species of insects, arachnids, shellfish, and crustaceans that secrete silk-like protein filaments that may provide easier-to-process or higher performance silks. Biotechnology also allows for the modification of proteins or polymers to impart unique high performance properties.

Because of the relative nascency of this technology, one of the current challenges with this bottom-up recombinant protein approach is the cost and scale of fermentation processes. Recombinant protein synthesis first found success in the pharmaceutical space, where low volume, high value products enabled even expensive, low yield protein synthesis to enter the market.<sup>142</sup> However, advancements in cellular engineering and fermentation processes have now enabled higher volume, lower value products such as raw chemicals, food ingredients, and now biopolymers such as silk proteins to be realized.

### Figure 25. Strategies to create synthetic copolymers that mimic silk.



Source: Amrita Sarkar et al., "Chemical Synthesis of Silk-Mimetic Polymers," Materials 12, 4086 (2019): 8.

Silk proteins, for example, could be enhanced with new properties such as water repellency through the incorporation of nanoparticles or by reacting the protein functional groups to form new chemical moieties on the surface.<sup>141</sup>



The science behind synthetic protein synthesis is still relatively new. While fermentation of microbes to produce molecules such as alcohol emerged early in history, the ability to engineer organisms to produce bespoke products they didn't evolve to produce is a recent scientific advancement. Recombinant organisms and resultant protein synthesis was first discovered in the 1970s.<sup>143</sup>

Genome editing of broad classes of organisms has only recently entered its "revolution" due to the advancements possible with CRISPR Cas9 editing tools, for which the Nobel Prize in Chemistry was awarded in 2020.<sup>144</sup> Even more recent advancements have enabled cell-free protein synthesis, whereby crude cellular extracts such as amino acids, RNA/DNA, and enzymes can be manipulated to form de novo proteins without the cell itself.<sup>145</sup> At the end of 2020, Google-owned, DeepMind announced their advancement in the rapid solving of unknown protein structures assisted by artificial intelligence. Their AlphaFold technology revealed in 30 minutes the structure of a protein that researchers had been trying to figure out for 10 years.<sup>146</sup> Many more bioengineering and synthetic biology advancements are happening in real time, and these will enable faster, more costeffective approaches that harness biology to create novel materials such as recombinant silk.

"Spider silk is renowned for its amazing toughness; however, spiders are cannibalistic and cannot be farmed, and consequently, synthetic spider silk possessing the extraordinary strength and flexibility of spider silk in nature has long been perceived as the Holy Grail of material science. Needless to say, when I learned that Hebrew University had patented a self-generating synthetic spider silk, I jumped at the opportunity to license this new material, which gave rise to Seevix. After seven years of painstaking R&D, Seevix has established that its synthetic spider silk, SVX™, indeed possesses the remarkable characteristics of natural spider silk and can be combined in small percentages with other materials to significantly enhance their toughness. Equally important, Seevix has discovered how to manufacture animal-free, biodegradable SVX™ in industrial quantities and at a fraction of its original cost, resulting in collaborations with leading multinational companies which are seeking sustainable, high-performance alternatives to existing polymers."

- Dr. Shlomzion Shen, Co-Founder & CEO, Seevix Material Science

Bioengineering and synthetic biology advancements are happening in real time, and these will enable faster, more cost-effective approaches that harness biology to create novel materials such as recombinant silk.



Figure 26. The natural spinning process of silk in spiders (top) compared with synthetic silk spinning approaches of recombinant silk protein (bottom).

Source: Whittall, D.R., et al. Host Systems for the Production of Recombinant Spider Silk. Trends in Biotechnology. 2020. https://www.cell.com/trends/biotechnology/fulltext/S0167-7799(20)30244-4

Another bottom-up technique is rational polymeric design. This technique replicates the complex structure and properties of the silk protein and resultant fiber, including the use of synthetic copolymers or polymer-peptide hybrids.<sup>147</sup> The structure of the silk protein with its alternating "blocks" of crystalline and amorphous segments, can be mimicked with synthetic polymers that form similar structures (Figure 25). Nearly all rational polymeric design approaches have been limited to academic research and not yet applied to commercial scale silk fibers for fabric applications. Challenges include 1) synthesis strategies for the high molecular weight (i.e., long chain) polymers needed to impart desirable mechanical properties, and 2) strategies to increase synthetic polymer solubility to enable fiber processing.148

For recombinant protein and synthetic silk mimetics, the greatest challenge is the transformation of the chemical components into the complex structure that is key to silk's unique properties. For recombinant proteins, the complex folding, assembly, crystallization, and alignment are difficult to replicate in the lab. For synthetic copolymers or peptide hybrids, the solubility<sup>149</sup> of the polymer is the challenge. In order to perform the wet spinning process, which is necessary to form the fiber from these raw materials, the protein or synthetic polymer must be dissolved in solution, and current chemistries have limited solubility.<sup>150</sup> It is also challenging to spin the dope and provide elongational forces in the form of draw to obtain the structure necessary for silk's unique properties (Figure 26).

"The uniqueness of silk is palpable. Spidey Tek's spider silk is stronger, lighter, more carbon neutral and more sustainable than steel, aluminum, carbon fiber and/or other materials utilized heavily in current industries."

- Roberto Velozzi, Chairman & CEO of Spidey Tek.

Figure 27. Orange Fiber fibers derived from citrus waste

"It is possible to make silk proteins synthetically, but it is very hard to assemble the individual proteins into a fiber or other material forms. The spider has a complex spinning duct in which silk proteins are exposed to physical forces, chemical gradients, the combination of which generates the assembly of molecules that leads to silk fibers."

#### - Markus Buehler, MIT Professor.

Source: https://singularityhub.com/2019/04/11/thetangled-web-of-turning-spider-silk-into-a-super-material/

#### **TOP-DOWN MATERIALS DESIGN:**

Top-down material design typically involves finding naturally occurring or synthetic materials that closely mimic the performance of silk fiber. These materials may already be readily available or require minimal alteration. The top-down approach is typically a faster way to create commercial scale fibers than bottom-up approaches. However, the top-down approach may have limitations in its ability to mimic all of silk's desirable qualities. One top-down approach uses naturally occurring plant fibers as a replacement for silk. As silk is the only naturally-occurring continuous filament fiber, attempts to use plant fibers have generally fallen short.

Figure 28. An image of spider silk fabric created by Spiber. Credit: Spiber, Inc.

"Silk is nature's protein-based fiber, and evolved naturally long before even Nylon's invention. Now with the technology to custom design protein polymers, we can use the template provided by Nature to create versions of silk that overcome its limitations — both in performance and sustainability — for use as alternatives to the petroleumbased polymers we've become dependent on for apparel."

- David Breslauer, Bolt Thread's Chief Scientific Officer

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Strategies to increase the molecular weight and solubility of synthetic silk-mimetic polymers could overcome current process challenges.<sup>148</sup> Continued innovation is needed in order to reduce the environmental footprint of these "current gen" fibers without sacrificing performance.

# WS

An obvious point of entry for next-gen silk innovation would be to improve upon the performance and environmental footprint of current silk replacements, including cellulosics, nylon, and polyester. Closed-loop chemical processes and the use of agricultural waste have led to improvements in the environmental footprint of cellulosic materials such as rayon (also known as viscose).<sup>151</sup> Partial bio-based materials, made with plant-derived feedstocks and novel biodegradable chemistries, have begun to enter the market.

#### **CURRENT INNOVATORS**

An overview of the two categories of sustainable silk fiber replacements and examples of current innovators in this space.

### Bottom-up: Recombinant protein synthesis to produce protein-based fibers

- Spiber: Brewed Protein (Figure 28)
- AM Silk: Biosteel
- Bolt Threads: Microsilk
- Seevix: SVX
- Spidey Tek

#### **Top-down: Cellulose-based fiber technology**

- ENKA Viscose: regenerated cellulose fiber derived from sustainably sourced Northern European conifers
- Orange Fiber: cellulose extracted from citrus waste and chemically processed into acetylated cellulose fibers, which may be blended with other fabrics (Figure 27)
- SmartFiber AG: SeaCell, SmartCell: cellulose derived fibers formed from the Lyocell process with zinc oxide and seaweed additives

#### **CHALLENGES & OPPORTUNITIES**

Regardless of the replacement approach, the conversion of raw material to fiber or yarn is a big technical challenge. Producing nearly identical silk protein via precision fermentation technology has been successful, but the unique assembly process that happens in the spinning dope in the gland of the animal is difficult to replicate. Like baking a souffle, ingredients are just one part of the process. Dissolving the protein, and then tightly controlling pH, crystallization, fibril formation and alignment, production of core-sheath structure, and drying the resulting fiber all happen simultaneously in animal-derived silk production. To replicate this synchrony during the synthetic spinning of recombinant silk protein is extremely challenging. Similarly, processing silk mimicking synthetic polymers or peptide-polymer hybrids is difficult due to the lack of solubility of these polymers for wet spinning methods. Sustainability also remains a concern: avoidance of hazardous chemicals and of excessive water and energy use is necessary for next-gen silk production to succeed as a sustainable alternative.

Overcoming Challenges: Innovator Spiber has collaborated on scientific literature related to novel water-based spinning systems for conversion of the silk dope to fibers with high toughness and elongation at break.<sup>152</sup>



Source: https://boltthreads.com/technology/microsilk/

Left: Bolt Threads Microsilk™ fabric in the MoMA dress by Stella McCartney Right: Orange Fiber's next-gen silk was featured in the H&M Conscious Exclusive Collection 2019 The future of next-gen silk may actually allow for plastic-eating microbes to create silk, thus reducing plastic waste while creating animal-free silk!

"Our research develops genetically modified bacteria capable of producing recombinant silk protein by metabolizing waste plastic. At some point, we as a society should be transitioning to using plastics that not only come from nonpetroleum-based sources, but can also completely degrade into something that goes into the natural environment. While some of the materials produced may replace [textile] silk, the intention of the project is to develop a microbial system that can produce silk materials with tunable properties that may suit a diverse range of applications."

- Professor Helen Zha, Ph.D., Rensselaer Polytechnic Institute.

 $\label{eq:source:https://www.plasticstoday.com/materials-research/research-turns-plastic-waste-biodegradable-silk$ 



Source: http://orangefiber.it/en/collections/

Regardless, there is great opportunity for both bottom-up and top-down material design approaches to disrupt the silk market. Novel suites of sustainable synthetic polymers, natural proteins, or hybrid materials could act not only as replacements for silk, but for some of the other fibers on the market such as polyester, rayon, or cotton. But why start with silk as a target? Many point to silk being <1% of the textile fibers produced annually, while polyester is >50%, so why not focus on polyester?<sup>153</sup> Here are just a few of the reasons why innovation in silk is a great opportunity:

#### • SMALL VOLUME, BIG IMPACT

The smaller global production could be a good thing for early innovators. To produce 5% of the annual global production of silk, one would only need to produce 8000 tons of silk. To do the same for polyester, one would need to produce 2,850,000 tons of polyester. Even early production runs by a silk-replacement start-up can make a huge impact on market volume.<sup>154</sup>

#### • LUXURY, HIGH VALUE

Silk is a luxury material with a much greater profit margin than polyester. Raw silk (3A grade) costs \$53/kg, while polyester filament yarn costs ~\$1/kg.<sup>155</sup> The higher profit could enable technology with relatively high production costs such as precision fermentation to get closer to price parity. The current silk market is projected at ~\$17 billion.<sup>156</sup>

#### • NOVEL MATERIAL, NEW MARKETS

Recombinant silks, such as those from spiders or other species, are currently an untapped market for textiles as they cannot be harvested naturally. Creating some of the strongest and toughest textile fibers in existence, replacements for silk could enter new markets such as military applications, sports apparel, outdoor wear, and technical textile applications.

#### • LESS COMPETITION

While key players are beginning to emerge, the next-gen silk space is not crowded. Competing with the global chemical powerhouses that manufacture polyester could be a daunting undertaking.

#### • A STEPPING STONE TO SYNTHETICS

If synthetics are currently used as silk replacements, then a novel high performing silk replacement could also replace synthetics. The entirety of global fiber production, >100 million metric tons annually, is an innovator's playground.

# Look for MII's upcoming report on the state of the industry for insights on the next-gen material space!

One question for innovators to keep in mind, particularly for the use of silk in fashion or homegoods: does silk *need* all the properties it currently has? In many ways, the fiber may be "overengineered" for fashion applications. We don't necessarily need the fibers that go into blouses or scarves to have mechanical properties that exceed those of Kevlar, as spider silk fibers do. The current pipeline of research on silk replacements may be optimized for mechanics or biocompatibility, in order to be applied to engineering or medical applications. Different characteristics such as aesthetics, workability, durability, and comfort are needed for fashion and homegoods applications, and innovators should keep these in mind. The stellar mechanical properties of spider silk should be considered for performance and outerwear applications, as strong and tough fibers are required. Recombinant spider silk innovation may enable silk to enter new submarkets.

### SUMMARY: KEY TARGETS FOR CREATING SILK ALTERNATIVES



Throughout this report, we have identified key aspects of silk that give rise to its aesthetic and performance features. We have also described ways that silk could be improved, or ways that next-gen silk could apply to broader applications. Highlights for those targets to match or exceed silk properties are outlined below.

#### TO MEET THE PERFORMANCE OF CURRENT COMMERCIAL SILK:

#### FIBER PROPERTIES

- Continuous filament
- Translucency and triangular cross-section, prismatic fiber for luster
- Fine (low denier, small diameter) fibers
- Hierarchical structure, crystallinity, and alignment to impart strength and toughness
- Low density
- Proccessable into yarn, fabric

#### FABRIC PROPERTIES

- Soft handfeel
- Fluid drape
- "Scroop" the signature silk sound
- Comfort absorbent in warm weather, insulation in cold weather, triangular fiber does not sit against skin
- Lightweight
- Pilling and abrasion resistance
- Flame retardant

#### TO IMPROVE UPON THE PERFORMANCE OF SILK AND OPEN UP NEW APPLICATIONS:

- ELIMINATE THE USE OF ANIMALS
- DECREASE ENVIRONMENTAL FOOTPRINT
- INCREASE UV RESISTANCE
- DECREASE TENDENCY FOR STATIC BUILD UP
- INCREASE PROCESSABILITY
- INCREASE CHEMICAL/WATER/STAIN RESISTANCE
- DECREASE SHRINKAGE
- INCREASE LAUNDERABILITY
- DECREASE COST
- INCREASED MECHANICAL PROPERTIES FOR HIGH PERFORMANCE APPLICATIONS
- INCREASE DURABILITY

"Fashion has long relied on farming, for better or for worse, to supply luxury materials like silk. However, we are now on the cusp of creating another more sustainable bridge to fashion for these materials and this time it is coming from the lab. There could not be a more exciting time to be involved in science and fashion."

- Thomasine Dolan, Fashion Design Specialist, Material Innovation Initiative



Silk, the Queen of Fibers, remains one of the most luxurious materials used in the fashion and home goods industries. However, the trillion silkworms killed annually, and the damaging environmental impact associated with silk's production, leave much to be desired. Current silk replacements, such as polyester, nylon, and rayon, have their own environmental concerns. In this era of unparalleled materials and manufacturing innovation, we now have the ability to match the performance and aesthetics of silk without relying on animal agriculture. By understanding the science of silk and how it relates to its unique properties, innovators have the opportunity to transform the fiber market with sustainable silk alternatives. The time is right for a new Queen of Fibers in the form of next-gen silk.

# **APPENDIX I. LIFE CYCLE ANALYSIS** (LCA) DETAILS FOR SILK

The following data provides detail on LCA process share from the data presented in Table 1. This data is based on a case study of silk production in India and may not be representative of all silk production.

#### Table A1. Share of environmental impact of silk by process.<sup>157</sup>

	Global warming potential (100 years; kg CO2 <sub>eq</sub> / kg)	Cumulative energy demand (renewable; MJ/ kg)	Cumulative energy demand (nonrenewable; MJ/kg)	Agricultural land occupation (m²a/kg)	Freshwater eutrophication (g P <sub>eq</sub> /kg)	Blue water footprint (m³/kg)	Ecotoxicity (CTU <sub>e</sub> /kg)
Mulberry field	28%ª	74% <sup>b</sup>		62%	50%ª		97%
Composting	17%						
Irrigation	11%°		34%°		9%	37% <sup>d</sup> ; 62%e	
Fertilizer manufacture	8%				18%		
Field operations	5%						
Cocoon drying	18%°		58%°		14%		
Cocoon reeling		25% <sup>f</sup>	5%	37% <sup>f</sup>			
Other	13%	1%	4%	1%	11%		3%
Total	51.5	1349.9	110.1	19.7	4.8	24.6	522.8

<sup>a</sup>Field emissions from fertilization, <sup>b</sup>solar energy requirement, <sup>c</sup>electricity, <sup>d</sup>groundwater, <sup>e</sup>surface, <sup>f</sup>firewood provision.

### APPENDIX II. EXAMPLE PERFORMANCE CRITERIA FOR SILK FABRIC

Example of expected performance specification of woven silk fabrics for a fashion retailer. Apparel includes shirts, blouses, dresses, skirts, pants, jackets.<sup>158</sup> This information is provided as an example and is not intended to reflect the performance requirements of silk in all applications.

#### Table A2. Example performance specification for silk apparel.

Test	Example Test Method	
Flammability	16 CFR Part 1610	Class 1
Dimensional Stability	AATCC 135/150 (after three machine washings)	3% max for length and width 2% max for length and width
Skew	AATCC 158 (after one dry cleaning)	3% max
Tensile Strength (warp & fill)	ASTM D5034	<68 g/m²: 15 lbs tops + bottoms 68-135 g/m²: 25 lbs tops + bottoms >135 g/m2²: 30 lbs tops, 35 lbs bottoms
Tear Strength (warp & fill)	ASTM D1424	<68 g/m²: 1.5 lbs tops + bottoms >68 g/m²: 2 lbs tops, 2.5 lbs bottoms
Seam Strength	ASTM D1683	<68 g/m²: 15 lbs >68 g/m²: 25 lbs
Seam Slippage	ASTM D1683 using existing seams	Tops: 15 lbs @ ¼" Bottoms: 25 lbs @ ¼"
Abrasion Resistance	ASTM D4966	Class 4.0 after 10,000 cycles
Pilling Resistance	ASTM D4970	Class 4.0 after 100 cycles
Perspiration	AATCC 15	Color change: Class 4.5 Staining: Class 4.0
Crocking	AATCC 8/116	Light-Medium: 4.0 dry, 3.0 wet Dark: 3.5 dry, 2.5 wet Special: 3.5 dry, 2.0 wet
Colorfastness to non-chlorine bleach	ASTM/AATCC TS-001	Color change: Class 4.0
Colorfastness to Laundering	AATCC 61/132	Color Change: 4.0 Staining: 4.0 Self-Staining: 4.5 (for Light-Medium, Dark, & Special)
Colorfastness to Dry Cleaning	AATCC 132	Color Change: 3.5 Staining: 4.0 Self-Staining: 4.5 (for Light-Medium, Dark, & Special)
Lightfastness (10 hours AFU exposure)	AATCC 16 E	Light-Medium, Color Change: 3.5 Dark, Color Change: 4.0 Special ,Color Change: 4.0
pH level	AATCC 81	pH 6-8
Formaldehyde	AATCC 112	75 ppm

# APPENDIX III. MICROSCOPY OF SILK FABRICS

Figure A1: Optical microscopy of various silk fabric samples, with 20x magnification on the left and 200x magnification on the right. Note the influence of yarn and weave structure (apparent at 200x), on the high level visual appearance (apparent at 20x). Scale bar 200 microns.



Figure A2. Optical microscopy of chiffon fabric made from polyester (left) and silk (right), demonstrating that polyester can achieve similar structure and aesthetics to silk. Scale bar 200 microns.



Figure A3. Optical microscopy of cotton/polyester blend (left) and 100% cotton fabric (right). Note the frequent appearance of free fibers, characteristic of staple yarns, compared with the filament yarn of silks shown in previous images above. Scale bar 200 microns.

![](_page_52_Figure_3.jpeg)

Figure A4. Optical microscopy of silk, polyester, and cotton fabrics, focusing on the yarn at cut edges of the fabric. All insets (blue) shown at same scale, highlighting the relative size and shape of the fibers in the yarn. Note that the silk fabric yarns contain the finest fibers. The cotton fibers have a characteristic "twist" and non-uniform cross section. The two different polyester fabrics show that a variety of diameters and morphologies are possible with polyester fibers. Overall images at 200x, scale bar 200 microns.

Silk crepe de chine

![](_page_53_Picture_2.jpeg)

100% cotton fabric

![](_page_53_Picture_4.jpeg)

Polyester satin

Polyester chiffon

![](_page_53_Picture_8.jpeg)

![](_page_53_Picture_9.jpeg)

![](_page_53_Picture_10.jpeg)

![](_page_53_Picture_11.jpeg)

MII would like to thank the laboratory of Prof. Jennifer Lewis, Sc.D. at Harvard University for equipment access to obtain these images.

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#### **ABOUT MII**

The Material Innovation Initiative is a nonprofit that accelerates the development of "next-gen" (high performance, animal-free, and more sustainable) materials for the fashion, automotive, and home goods industries. Technological innovation and untapped natural materials have the potential to transform the materials industry and solve the enormous environmental challenges it faces.

We work for materials that can do more, while requiring less of the planet, animals, and people involved at every stage. We imagine a circular future where the default choice for your sweater, sneaker, or seat is humane and sustainable; a future where animals are allowed to live free and thrive, where the planet is saved from pollution and degradation, and where workers are treated fairly and with respect.

MII's team of experts advance innovation in three main ways:

- 1. identifying and assessing innovative materials and technologies;
- 2. spurring investments, research, and development to scale innovations; and
- 3. partnering with brands, retailers, and suppliers to get sustainable materials to market.

We work with scientists, entrepreneurs, investors, material companies, and brands. Please reach out to us to get involved.

![](_page_61_Picture_8.jpeg)

**Nicole Rawling** 

![](_page_61_Picture_9.jpeg)

![](_page_61_Picture_10.jpeg)

Sydney Gladman

![](_page_61_Picture_11.jpeg)

Elaine Siu

![](_page_61_Picture_12.jpeg)

Jacqueline

Kravette

![](_page_61_Picture_13.jpeg)

Lisa Lupinski

![](_page_61_Picture_14.jpeg)

![](_page_61_Picture_15.jpeg)

**Jonathan Frappier** 

![](_page_61_Picture_17.jpeg)

![](_page_61_Picture_18.jpeg)

![](_page_61_Picture_19.jpeg)

![](_page_61_Picture_20.jpeg)

![](_page_61_Picture_21.jpeg)

![](_page_61_Picture_22.jpeg)

Joshua Hanosh

![](_page_61_Picture_24.jpeg)

**Cortney Busch** 

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![](_page_61_Picture_32.jpeg)

![](_page_61_Picture_33.jpeg)

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