

CHEMICALLY LINKED SILK FIBROIN COATINGS AND METHODS OF MAKING AND USING THEREOF

FIELD

The disclosure relates to chemically linked silk fibroin coatings and methods of making and using thereof, for example use of such chemically linked fibroin in coated articles, including various fabric and leather apparel, and various fabric and leather products for use in home and automotive applications.

BACKGROUND

Silk is a natural polymer produced by a variety of insects and spiders, and comprises a filament core protein, silk fibroin, and a glue-like coating consisting of a non-filamentous protein, sericin. Silk fibers are light weight, breathable, and hypoallergenic. Silk is comfortable when worn next to the skin and insulates very well; keeping the wearer warm in cold temperatures and is cooler than many other fabrics in warm temperatures.

SUMMARY

The disclosure relates to articles including one or more coated substrates, wherein the coatings include silk protein fragments (SPF) as defined herein, including without limitation silk fibroin or silk fibroin fragments, and a chemical modifier or a physical modifier. In some embodiments, the chemical modifier is chemically linked to one or more of a silk fibroin side group and a silk fibroin terminal group. In some embodiments, the silk fibroin side group and the silk fibroin terminal group are independently selected from an amine group, an amide group, a carboxyl group, a hydroxyl group, a thiol group, and a sulfhydryl group. In some embodiments, the chemical modifier is chemically linked to one or more functional groups on the substrate. In some embodiments, the functional group on the substrate is selected from an amine group, an amide group, a carboxyl group, a hydroxyl group, a thiol group, and a sulfhydryl group. In some embodiments, the chemical modifier includes one or more of a chemically linked functional group, or functional group residue, and a linker. In some embodiments, the chemical modifier includes one or more of $-CR^a_2-$, $-CR^a=CR^a-$, $-C\equiv C-$, $-alkyl-$, $-alkenyl-$, $-alkynyl-$, $-aryl-$,

-heteroaryl-, -O-, -S-, -OC(O)-, -N(R^a)-, -N=N-, =N-, -C(O)-, -C(O)O-, -OC(O)N(R^a)-, -C(O)N(R^a)-, -N(R^a)C(O)O-, -N(R^a)C(O)-, -N(R^a)C(O)N(R^a)-, -N(R^a)C(NR^a)N(R^a)-, -N(R^a)S(O)_t-, -S(O)_tO-, -S(O)_tN(R^a)-, -S(O)_tN(R^a)C(O)-, -OP(O)(OR^a)O-, wherein t is 1 or 2, and wherein at each independent occurrence R^a is selected from hydrogen, alkyl, alkenyl, fluoroalkyl, carbocyclyl, carbocyclylalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl, or heteroarylalkyl. In some embodiments, the coating includes one or more of low molecular weight silk fibroin or silk fibroin fragments, medium molecular weight silk fibroin or silk fibroin fragments and high molecular weight silk fibroin or silk fibroin fragments. In some embodiments, the coating includes SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, with an average weight average molecular weight from about 5 to about 144 kDa. In some embodiments, the coating includes SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, with an average weight average molecular weight from about 1 kDa to about 5 kDa, from about 5 kDa to about 10 kDa, from about 6 kDa to about 17 kDa, from about 10 kDa to about 15 kDa, from about 15 kDa to about 20 kDa, from about 17 kDa to about 39 kDa, from about 20 kDa to about 25 kDa, from about 25 kDa to about 30 kDa, from about 30 kDa to about 35 kDa, from about 35 kDa to about 40 kDa, from about 39 kDa to about 80 kDa, from about 40 kDa to about 45 kDa, from about 45 kDa to about 50 kDa, from about 60 kDa to about 100 kDa, or from about 80 kDa to about 144 kDa. In some embodiments, the coating includes SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, with a polydispersity between 1 and about 5.0. In some embodiments, the coating includes SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, which prior to coating the substrate are stable in a solution. In some embodiments, the coating includes SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, which prior to coating the substrate do not spontaneously or gradually gelate and/or do not visibly change in color or turbidity when in a solution for at least 10 days. In some embodiments, the substrate includes one or more of a fiber, a thread, a yarn, a fabric, a textile, a cloth, or a hide. In some embodiments, the fabric, textile, or cloth is woven or nonwoven. In some embodiments, the fiber, thread, or yarn includes one or more of polyester, recycled polyester, Mylar, cotton, nylon, recycled nylon,

polyester-polyurethane copolymer, rayon, acetate, aramid (aromatic polyamide), acrylic, ingeo (polylactide), lurex (polyamide-polyester), olefin (polyethylene-polypropylene), and combinations thereof. In some embodiments, the fiber, thread, or yarn includes one or more of alpaca fiber, alpaca fleece, alpaca wool, lama fiber, lama fleece, lama wool, cotton, cashmere, sheep fiber, sheep fleece, sheep wool, byssus, chiengora, qiviut, yak, rabbit, lambswool, mohair wool, camel hair, angora wool, silkworm silk, abaca fiber, coir fiber, flax fiber, jute fiber, kapok fiber, kenaf fiber, raffia fiber, bamboo fiber, hemp, modal fiber, pina, ramie, sisal, and soy protein fiber. In some embodiments, the fiber, thread, or yarn includes one or more of mineral wool, mineral cotton, man-made mineral fiber, fiberglass, glass, glasswool, stone wool, rock wool, slagwool, glass filaments, asbestos fibers, and ceramic fibers.

The disclosure also relates to a method of coating a substrate with a coating including SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, and a chemical modifier or a physical modifier, the method including applying to the substrate at least one composition including SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, with an average weight average molecular weight from about 1 kDa to about 144 kDa, and a polydispersity between 1 and about 5.0. In some embodiments, the method further includes applying to the substrate a chemical modifier or a physical modifier selected from a wetting agent, a detergent, a sequestering or dispersing agent, an enzyme, a bleaching agent, an antifoaming agent, an anti-creasing agent, a dye dispersing agent, a dye leveling agent, a dye fixing agent, a dye special resin agent, a dye anti-reducing agent, a pigment dye system anti-migrating agent, a pigment dye system binder, a delave agent, a wrinkle free treatment, a softener, a handle modifier, a waterborne polyurethane dispersion, a finishing resin, an oil or water repellant, a flame retardant, a crosslinker, an activator, a thickener for technical finishing, or any combination thereof. In some embodiments, the crosslinker or the activator are independently selected from a N-hydroxysuccinimide ester crosslinker, an imidoester crosslinker, a sulfosuccinimidyl aminobenzoate, a methacrylate, a silane, a silicate, an alkyne compound, an azide compound, an aldehyde, a carbodiimide crosslinker, a dicyclohexyl carbodiimide activator, a dicyclohexyl carbodiimide crosslinker, a maleimide crosslinker, a haloacetyl crosslinker, a pyridyl

disulfide crosslinker, a hydrazide crosslinker, an alkoxyamine crosslinker, a reductive amination crosslinker, an aryl azide crosslinker, a diazine crosslinker, an azide-phosphine crosslinker, a transferase crosslinker, a hydrolase crosslinker, a transglutaminase crosslinker, a peptidase crosslinker, an oxidoreductase crosslinker, a tyrosinase crosslinker, a laccase crosslinker, a peroxidase crosslinker, a lysyl oxidase crosslinker, and combinations thereof. In some embodiments, the composition includes low molecular weight SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments. In some embodiments, the composition includes medium molecular weight SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments. In some embodiments, the composition includes high molecular weight SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments. In some embodiments, the composition includes a chemical fabric softener. In some embodiments, the composition includes a Brønsted acid. In some embodiments, the method further includes dyeing the substrate prior to applying to the substrate the at least one composition including SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments. In some embodiments, the method further includes dyeing the substrate after applying to the substrate the at least one composition including SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments.

The disclosure also relates to a method of coating a substrate with a coating including SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, and a chemical modifier or a physical modifier, for example a crosslinker, the method including applying to the substrate at least one composition including SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, with an average weight average molecular weight from about 1 kDa to about 144 kDa, and a polydispersity between 1 and about 5.0, wherein the chemical modifier or physical modifier, for example the crosslinker, is added “in-situ,” i.e., at the same time the SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, are added to the substrate, for example a fabric.

The disclosure also relates to a method of coating a substrate with a coating including SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, and a chemical modifier or a physical modifier, for example a crosslinker, the

method including applying to the substrate at least one composition including SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, with an average weight average molecular weight from about 1 kDa to about 144 kDa, and a polydispersity between 1 and about 5.0, wherein the chemical modifier or physical modifier, for example the crosslinker, is added to the SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, to create a modified silk fibroin, which is thereafter applied to the substrate, for example a fabric.

The disclosure relates to articles including one or more coated substrates, the articles including, but not being limited to, apparel, padding, shoes, gloves, luggage, furs, jewelry and bags, configured to be worn or carried on the body, that is at least partially surface treated with a composition, for example a solution, of pure silk fibroin-based protein fragments of the present disclosure so as to result in a silk coating on the product. In some embodiments, the solutions of silk fibroin-based proteins or fragments thereof may be aqueous solutions, organic solutions, or emulsions. In an embodiment, the product is manufactured from a textile material. In an embodiment, the product is manufactured from a non-textile material. In an embodiment, desired additives can be added to an aqueous solution of pure silk fibroin-based protein fragments of the present disclosure so as to result in a silk coating having desired additives.

BRIEF DESCRIPTION OF THE DRAWINGS

The presently disclosed embodiments will be further explained with reference to the attached drawings. The drawings shown are not necessarily to scale, with emphasis instead generally being placed upon illustrating the principles of the presently disclosed embodiments.

Fig. 1A illustrates a synthetic scheme for conjugating silk fibroin to a reactive linker, which is then reacted to a group on a substrate. Fig. 1B illustrates a synthetic scheme for chemical modification and purification of silk molecules; the pH of the silk solutions was 7-8 prior to addition of crosslinker; the pH dropped significantly upon addition of the crosslinker; the pH was then adjusted to 8.5, and the samples were either dialyzed against water or purified via TFF against water; the pH was adjusted to 4-5 for fabric coatings. Fig. 1C illustrates a synthetic scheme for in situ modification of silk; the

pH of the silk solutions was 6-7 prior to addition of crosslinker; the pH dropped significantly upon addition of the crosslinker; the solution was filtered and used within hours for fabric coatings without purification or pH adjustments.

Fig. 2 illustrates some examples of chemically linked Silk-Substrate constructs, including Silk-Linker-Substrate constructs.

Fig. 3 illustrates a synthetic scheme for conjugating a substrate to a reactive linker, which is then reacted to silk fibroin; several Silk-Linker-Substrate constructs are depicted including an amino-silane based linker.

Figs. 4A and 4B illustrate comparative vertical wicking test results for samples coated with chemically modified silk fibroin (STI-17100706-D001: coated with silk-conjugate; STI-17100706-D002: coated with silk only; STI-17100706-D003: coated with precursor linker only; STI-17100706: control), tested after a number (T) of laundering cycles (T=0, Fig. 4A; T=3 Fig. 4B; samples coated with a silk-conjugate, and samples coated with silk only improve wicking compared to an unfinished control sample; samples coated with a silk-conjugate shows better wicking than samples coated with silk only; unfinished control samples, and samples coated with a precursor linker only show almost no wicking.

Figs. 5A and 5B illustrate comparative absorbency test results for samples coated with chemically modified silk fibroin (STI-17100706-D001: coated with silk-conjugate; STI-17100706-D002: coated with silk only; STI-17100706-D003: coated with precursor linker only; STI-17100706: control), tested after a number (T) of laundering cycles (T=0, Fig. 5A; T=3 Fig. 5B); samples coated with a silk-conjugate, and samples coated with silk only have a significantly improved absorbency, and samples coated with a silk-conjugate absorb better than samples coated with silk only; unfinished control samples and samples coated with the precursor linker only do not absorb for T=0.

Figs. 6A and 6B illustrate comparative dry rate test results for samples coated with chemically modified silk fibroin (STI-17100706-D001: coated with silk-conjugate; STI-17100706-D002: coated with silk only; STI-17100706-D003: coated with precursor linker only; STI-17100706: control), tested after a number (T) of laundering cycles (T=0, Fig. 6A; T=3 Fig. 6B); samples coated with a silk-conjugate have an improved dry rate compared to the unfinished sample; samples coated with silk only have lower dry rate

than unfinished control samples (Fig. 6A); for T=3 samples coated with a silk-conjugate show significant improvements (Fig. 6B).

Figs. 7A-7D illustrate comparative vertical wicking test results for samples coated with chemically modified silk fibroin (control: Fig. 7A; coated with silk only: Fig. 7B; coated with in-situ modified silk: Fig. 7C; coated with purified silk-conjugate: Fig. 7D), tested after a number (T) of laundering cycles (0, 3, and 20).

Figs. 8A-8D illustrate comparative absorbency test results for samples coated with chemically modified silk fibroin (control: Fig. 8A; coated with silk only: Fig. 8B; coated with in-situ modified silk: Fig. 8C; coated with purified silk-conjugate: Fig. 8D), tested after a number (T) of laundering cycles (0, 3, and 20).

Figs. 9A-9D illustrate comparative dry rate test results for samples coated with chemically modified silk fibroin (control: Fig. 9A; coated with silk only: Fig. 9B; coated with in-situ modified silk: Fig. 9C; coated with purified silk-conjugate: Fig. 9D), tested after a number (T) of laundering cycles (0, 3, and 20).

Fig. 10 illustrates comparative absorbency test results for samples coated with silk fibroin chemically modified with natural crosslinkers (control sample, sample coated with silk only, sample coated with silk modified with caffeic acid, sample coated with silk modified with genipin).

Figs. 11A-D illustrate the data analysis by PEAKS software for the mass spectrum obtained for functionalized silk samples: 077-027-1 (Fig. 11A), 077-024-2 (Fig. 11B), 077-028-2 (Fig. 11C) and 077-030-1 (Fig. 11D).

Figs. 12A-B show the electrophoresis gel for silk fibroin-based protein fragments (Fig. 12A), and functionalized silk fibroin-based protein fragments samples 077-024-2 (Lane 3), 077-027-1 (Lane 4), 077-027-2 (Lane 5), 077-028-2 (Lane 6), and 077-030-1 (Lane 7) (Fig. 12B). Lane 1 of Fig. 12B shows BioRad IEF Standards of molecular weight bands. Lane 2 of Fig. 12B shows IEF Sample buffer. Lane 8 of Fig. 12B shows MC-1. Lane 9 of Fig. 12B shows S700-SP. Lane 10 of Fig. 12B shows DBr-7. Lane 11 of Fig. 12B shows Ser-1. Fig. 12A shows the electrophoresis gel from several Activated Silks™, and Fig. 12B shows the electrophoresis gel for chemically modified Activated Silks™.

Fig. 13 shows the SEC-RI chromatograms of two modified Mid-MW silks (098-29-02, and 098-30-02) compared to an unmodified Mid-MW weight silk.

Fig. 14A-B show the m/z and ms2 fragmentation patterns for two subunits: heavy chain (Fig. 14A), light chain (Fig. 14B) in the mass spectra for the modified Low-MW silk (077-027-1).

Fig. 15A-C show the m/z and ms2 fragmentation patterns for all three subunits: heavy chain (Fig. 15A), light chain (Fig. 15B), and fibrohexamerin (Fig. 15C) in the mass spectra for the modified Low-MW silk (077-024-2).

Fig. 16 shows the m/z and ms2 fragmentation patterns light chain in the mass spectrum for the modified Low-MW silk (077-028-2).

Fig. 17 shows the m/z and ms2 fragmentation patterns light chain in the mass spectrum for the modified Low-MW silk (077-030-1).

Fig. 18 is a flow chart showing various embodiments for producing pure silk fibroin protein fragments (SPFs) of the present disclosure.

FIG. 19 is a flow chart showing various parameters that can be modified during the process of producing a silk protein fragment solution of the present disclosure during the extraction and the dissolution steps.

While the above-identified drawings set forth presently disclosed embodiments, other embodiments are also contemplated, as noted in the discussion. This disclosure presents illustrative embodiments by way of representation and not limitation. Numerous other modifications and embodiments can be devised by those skilled in the art which fall within the scope and spirit of the principles of the presently disclosed embodiments.

DETAILED DESCRIPTION

SPF Definitions and Properties

As used herein, “silk protein fragments” (SPF) include one or more of: “silk fibroin fragments” as defined herein; “recombinant silk fragments” as defined herein; “spider silk fragments” as defined herein; “silk fibroin-like protein fragments” as defined herein; and/or “chemically modified silk fragments” as defined herein. SPF may have any molecular weight values or ranges described herein, and any polydispersity values or ranges described herein. As used herein, in some embodiments the term “silk protein

fragment” also refers to a silk protein that comprises or consists of at least two identical repetitive units which each independently selected from naturally-occurring silk polypeptides or of variations thereof, amino acid sequences of naturally-occurring silk polypeptides, or of combinations of both.

SPF Molecular Weight and Polydispersity

In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from 6 kDa to 17 kDa. In an embodiment, a composition of the present disclosure includes SPF having a weight average molecular weight ranging from 17 kDa to 39 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from 39 kDa to 80 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 1 to about 5 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 5 to about 10 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 10 to about 15 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 15 to about 20 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 20 to about 25 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 25 to about 30 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 30 to about 35 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 35 to about 40 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 40 to about 45 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 45 to about 50 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average

weight average molecular weight ranging from about 50 to about 55 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 55 to about 60 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 60 to about 65 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 65 to about 70 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 70 to about 75 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 75 to about 80 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 80 to about 85 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 85 to about 90 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 90 to about 95 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 95 to about 100 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 100 to about 105 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 105 to about 110 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 110 to about 115 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 115 to about 120 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 120 to about 125 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 125 to about 130 kDa. In an

embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 130 to about 135 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 135 to about 140 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 140 to about 145 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 145 to about 150 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 150 to about 155 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 155 to about 160 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 160 to about 165 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 165 to about 170 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 170 to about 175 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 175 to about 180 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 180 to about 185 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 185 to about 190 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 190 to about 195 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 195 to about 200 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 200 to about 205 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average

weight average molecular weight ranging from about 205 to about 210 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 210 to about 215 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 215 to about 220 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 220 to about 225 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 225 to about 230 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 230 to about 235 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 235 to about 240 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 240 to about 245 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 245 to about 250 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 250 to about 255 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 255 to about 260 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 260 to about 265 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 265 to about 270 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 270 to about 275 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 275 to about 280 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 280 to about 285 kDa. In an

embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 285 to about 290 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 290 to about 295 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 295 to about 300 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 300 to about 305 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 305 to about 310 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 310 to about 315 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 315 to about 320 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 320 to about 325 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 325 to about 330 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 330 to about 335 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 335 to about 340 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 340 to about 345 kDa. In an embodiment, a composition of the present disclosure includes SPF having an average weight average molecular weight ranging from about 345 to about 350 kDa.

In some embodiments, compositions of the present disclosure include SPF compositions selected from compositions #1001 to #2450, having weight average molecular weights selected from about 1 kDa to about 145 kDa, and a polydispersity range selected from between 1 and about 5 (including, without limitation, a polydispersity of 1), between 1 and about 1.5 (including, without limitation, a

polydispersity of 1), between about 1.5 and about 2, between about 1.5 and about 3, between about 2 and about 2.5, between about 2.5 and about 3, between about 3 and about 3.5, between about 3.5 and about 4, between about 4 and about 4.5, and between about 4.5 and about 5:

PDI (about) MW (about)	1-5	1-1.5	1.5-2	1.5-3	2-2.5	2.5-3	3-3.5	3.5-4	4-4.5	4.5-5
1 kDa	1001	1002	1003	1004	1005	1006	1007	1008	1009	1010
2 kDa	1011	1012	1013	1014	1015	1016	1017	1018	1019	1020
3 kDa	1021	1022	1023	1024	1025	1026	1027	1028	1029	1030
4 kDa	1031	1032	1033	1034	1035	1036	1037	1038	1039	1040
5 kDa	1041	1042	1043	1044	1045	1046	1047	1048	1049	1050
6 kDa	1051	1052	1053	1054	1055	1056	1057	1058	1059	1060
7 kDa	1061	1062	1063	1064	1065	1066	1067	1068	1069	1070
8 kDa	1071	1072	1073	1074	1075	1076	1077	1078	1079	1080
9 kDa	1081	1082	1083	1084	1085	1086	1087	1088	1089	1090
10 kDa	1091	1092	1093	1094	1095	1096	1097	1098	1099	1100
11 kDa	1101	1102	1103	1104	1105	1106	1107	1108	1109	1110
12 kDa	1111	1112	1113	1114	1115	1116	1117	1118	1119	1120
13 kDa	1121	1122	1123	1124	1125	1126	1127	1128	1129	1130
14 kDa	1131	1132	1133	1134	1135	1136	1137	1138	1139	1140
15 kDa	1141	1142	1143	1144	1145	1146	1147	1148	1149	1150
16 kDa	1151	1152	1153	1154	1155	1156	1157	1158	1159	1160
17 kDa	1161	1162	1163	1164	1165	1166	1167	1168	1169	1170
18 kDa	1171	1172	1173	1174	1175	1176	1177	1178	1179	1180
19 kDa	1181	1182	1183	1184	1185	1186	1187	1188	1189	1190
20 kDa	1191	1192	1193	1194	1195	1196	1197	1198	1199	1200
21 kDa	1201	1202	1203	1204	1205	1206	1207	1208	1209	1210
22 kDa	1211	1212	1213	1214	1215	1216	1217	1218	1219	1220
23 kDa	1221	1222	1223	1224	1225	1226	1227	1228	1229	1230
24 kDa	1231	1232	1233	1234	1235	1236	1237	1238	1239	1240
25 kDa	1241	1242	1243	1244	1245	1246	1247	1248	1249	1250
26 kDa	1251	1252	1253	1254	1255	1256	1257	1258	1259	1260
27 kDa	1261	1262	1263	1264	1265	1266	1267	1268	1269	1270
28 kDa	1271	1272	1273	1274	1275	1276	1277	1278	1279	1280
29 kDa	1281	1282	1283	1284	1285	1286	1287	1288	1289	1290
30 kDa	1291	1292	1293	1294	1295	1296	1297	1298	1299	1300
31 kDa	1301	1302	1303	1304	1305	1306	1307	1308	1309	1310
32 kDa	1311	1312	1313	1314	1315	1316	1317	1318	1319	1320
33 kDa	1321	1322	1323	1324	1325	1326	1327	1328	1329	1330

34 kDa	1331	1332	1333	1334	1335	1336	1337	1338	1339	1340
35 kDa	1341	1342	1343	1344	1345	1346	1347	1348	1349	1350
36 kDa	1351	1352	1353	1354	1355	1356	1357	1358	1359	1360
37 kDa	1361	1362	1363	1364	1365	1366	1367	1368	1369	1370
38 kDa	1371	1372	1373	1374	1375	1376	1377	1378	1379	1380
39 kDa	1381	1382	1383	1384	1385	1386	1387	1388	1389	1390
40 kDa	1391	1392	1393	1394	1395	1396	1397	1398	1399	1400
41 kDa	1401	1402	1403	1404	1405	1406	1407	1408	1409	1410
42 kDa	1411	1412	1413	1414	1415	1416	1417	1418	1419	1420
43 kDa	1421	1422	1423	1424	1425	1426	1427	1428	1429	1430
44 kDa	1431	1432	1433	1434	1435	1436	1437	1438	1439	1440
45 kDa	1441	1442	1443	1444	1445	1446	1447	1448	1449	1450
46 kDa	1451	1452	1453	1454	1455	1456	1457	1458	1459	1460
47 kDa	1461	1462	1463	1464	1465	1466	1467	1468	1469	1470
48 kDa	1471	1472	1473	1474	1475	1476	1477	1478	1479	1480
49 kDa	1481	1482	1483	1484	1485	1486	1487	1488	1489	1490
50 kDa	1491	1492	1493	1494	1495	1496	1497	1498	1499	1500
51 kDa	1501	1502	1503	1504	1505	1506	1507	1508	1509	1510
52 kDa	1511	1512	1513	1514	1515	1516	1517	1518	1519	1520
53 kDa	1521	1522	1523	1524	1525	1526	1527	1528	1529	1530
54 kDa	1531	1532	1533	1534	1535	1536	1537	1538	1539	1540
55 kDa	1541	1542	1543	1544	1545	1546	1547	1548	1549	1550
56 kDa	1551	1552	1553	1554	1555	1556	1557	1558	1559	1560
57 kDa	1561	1562	1563	1564	1565	1566	1567	1568	1569	1570
58 kDa	1571	1572	1573	1574	1575	1576	1577	1578	1579	1580
59 kDa	1581	1582	1583	1584	1585	1586	1587	1588	1589	1590
60 kDa	1591	1592	1593	1594	1595	1596	1597	1598	1599	1600
61 kDa	1601	1602	1603	1604	1605	1606	1607	1608	1609	1610
62 kDa	1611	1612	1613	1614	1615	1616	1617	1618	1619	1620
63 kDa	1621	1622	1623	1624	1625	1626	1627	1628	1629	1630
64 kDa	1631	1632	1633	1634	1635	1636	1637	1638	1639	1640
65 kDa	1641	1642	1643	1644	1645	1646	1647	1648	1649	1650
66 kDa	1651	1652	1653	1654	1655	1656	1657	1658	1659	1660
67 kDa	1661	1662	1663	1664	1665	1666	1667	1668	1669	1670
68 kDa	1671	1672	1673	1674	1675	1676	1677	1678	1679	1680
69 kDa	1681	1682	1683	1684	1685	1686	1687	1688	1689	1690
70 kDa	1691	1692	1693	1694	1695	1696	1697	1698	1699	1700
71 kDa	1701	1702	1703	1704	1705	1706	1707	1708	1709	1710
72 kDa	1711	1712	1713	1714	1715	1716	1717	1718	1719	1720
73 kDa	1721	1722	1723	1724	1725	1726	1727	1728	1729	1730
74 kDa	1731	1732	1733	1734	1735	1736	1737	1738	1739	1740
75 kDa	1741	1742	1743	1744	1745	1746	1747	1748	1749	1750
76 kDa	1751	1752	1753	1754	1755	1756	1757	1758	1759	1760

77 kDa	1761	1762	1763	1764	1765	1766	1767	1768	1769	1770
78 kDa	1771	1772	1773	1774	1775	1776	1777	1778	1779	1780
79 kDa	1781	1782	1783	1784	1785	1786	1787	1788	1789	1790
80 kDa	1791	1792	1793	1794	1795	1796	1797	1798	1799	1800
81 kDa	1801	1802	1803	1804	1805	1806	1807	1808	1809	1810
82 kDa	1811	1812	1813	1814	1815	1816	1817	1818	1819	1820
83 kDa	1821	1822	1823	1824	1825	1826	1827	1828	1829	1830
84 kDa	1831	1832	1833	1834	1835	1836	1837	1838	1839	1840
85 kDa	1841	1842	1843	1844	1845	1846	1847	1848	1849	1850
86 kDa	1851	1852	1853	1854	1855	1856	1857	1858	1859	1860
87 kDa	1861	1862	1863	1864	1865	1866	1867	1868	1869	1870
88 kDa	1871	1872	1873	1874	1875	1876	1877	1878	1879	1880
89 kDa	1881	1882	1883	1884	1885	1886	1887	1888	1889	1890
90 kDa	1891	1892	1893	1894	1895	1896	1897	1898	1899	1900
91 kDa	1901	1902	1903	1904	1905	1906	1907	1908	1909	1910
92 kDa	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920
93 kDa	1921	1922	1923	1924	1925	1926	1927	1928	1929	1930
94 kDa	1931	1932	1933	1934	1935	1936	1937	1938	1939	1940
95 kDa	1941	1942	1943	1944	1945	1946	1947	1948	1949	1950
96 kDa	1951	1952	1953	1954	1955	1956	1957	1958	1959	1960
97 kDa	1961	1962	1963	1964	1965	1966	1967	1968	1969	1970
98 kDa	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980
99 kDa	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990
100 kDa	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
101 kDa	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010
102 kDa	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020
103 kDa	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030
104 kDa	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040
105 kDa	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050
106 kDa	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060
107 kDa	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070
108 kDa	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080
109 kDa	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090
110 kDa	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100
111 kDa	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110
112 kDa	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120
113 kDa	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130
114 kDa	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140
115 kDa	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150
116 kDa	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160
117 kDa	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170
118 kDa	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180
119 kDa	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190

120 kDa	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200
121 kDa	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210
122 kDa	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220
123 kDa	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230
124 kDa	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240
125 kDa	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250
126 kDa	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260
127 kDa	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270
128 kDa	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280
129 kDa	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290
130 kDa	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300
131 kDa	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310
132 kDa	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320
133 kDa	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330
134 kDa	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340
135 kDa	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350
136 kDa	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360
137 kDa	2361	2362	2363	2364	2365	2366	2367	2368	2369	2370
138 kDa	2371	2372	2373	2374	2375	2376	2377	2378	2379	2380
139 kDa	2381	2382	2383	2384	2385	2386	2387	2388	2389	2390
140 kDa	2391	2392	2393	2394	2395	2396	2397	2398	2399	2400
141 kDa	2401	2402	2403	2404	2405	2406	2407	2408	2409	2410
142 kDa	2411	2412	2413	2414	2415	2416	2417	2418	2419	2420
143 kDa	2421	2422	2423	2424	2425	2426	2427	2428	2429	2430
144 kDa	2431	2432	2433	2434	2435	2436	2437	2438	2439	2440
145 kDa	2441	2442	2443	2444	2445	2446	2447	2448	2449	2450

As used herein, “low molecular weight,” “low MW,” or “low-MW” SPF may include SPF having a weight average molecular weight, or average weight average molecular weight in a range of about 5 kDa to about 30 kDa, about 14 kDa to about 30 kDa, or about 6 kDa to about 17 kDa. In some embodiments, a target low molecular weight for certain SPF may be weight average molecular weight of about 5 kDa, about 6 kDa, about 7 kDa, about 8 kDa, about 9 kDa, about 10 kDa, about 11 kDa, about 12 kDa, about 13 kDa, about 14 kDa, about 15 kDa, about 16 kDa, about 17 kDa, about 18 kDa, about 19 kDa, about 20 kDa, about 21 kDa, about 22 kDa, about 23 kDa, about 24 kDa, about 25 kDa, about 26 kDa, about 27 kDa, about 28 kDa, about 29 kDa, or about 30 kDa.

As used herein, “medium molecular weight,” “medium MW,” or “mid-MW” SPF may include SPF having a weight average molecular weight, or average weight average molecular weight in a range of about 20 kDa to about 55 kDa, about 39 kDa to about 54 kDa, or about 17 kDa to about 39 kDa. In some embodiments, a target medium molecular weight for certain SPF may be weight average molecular weight of about 17 kDa, about 18 kDa, about 19 kDa, about 20 kDa, about 21 kDa, about 22 kDa, about 23 kDa, about 24 kDa, about 25 kDa, about 26 kDa, about 27 kDa, about 28 kDa, about 29 kDa, about 30 kDa, about 31 kDa, about 32 kDa, about 33 kDa, about 34 kDa, about 35 kDa, about 36 kDa, about 37 kDa, about 38 kDa, about 39 kDa, about 40 kDa, about 41 kDa, about 42 kDa, about 43 kDa, about 44 kDa, about 45 kDa, about 46 kDa, about 47 kDa, about 48 kDa, about 49 kDa, about 50 kDa, about 51 kDa, about 52 kDa, about 53 kDa, about 54 kDa, or about 55 kDa.

As used herein, “high molecular weight,” “high MW,” or “high-MW” SPF may include SPF having a weight average molecular weight, or average weight average molecular weight that is in a range of about 55 kDa to about 150 kDa, or about 39 kDa to about 80 kDa. In some embodiments, a target high molecular weight for certain SPF may be about 39 kDa, about 40 kDa, about 41 kDa, about 42 kDa, about 43 kDa, about 44 kDa, about 45 kDa, about 46 kDa, about 47 kDa, about 48 kDa, about 49 kDa, about 50 kDa, about 51 kDa, about 52 kDa, about 53 kDa, about 54 kDa, about 55 kDa, about 56 kDa, about 57 kDa, about 58 kDa, about 59 kDa, about 60 kDa, about 61 kDa, about 62 kDa, about 63 kDa, about 64 kDa, about 65 kDa, about 66 kDa, about 67 kDa, about 68 kDa, about 69 kDa, about 70 kDa, about 71 kDa, about 72 kDa, about 73 kDa, about 74 kDa, about 75 kDa, about 76 kDa, about 77 kDa, about 78 kDa, about 79 kDa, or about 80 kDa.

In some embodiments, the molecular weights described herein (e.g., low molecular weight silk, medium molecular weight silk, high molecular weight silk) may be converted to the approximate number of amino acids contained within the respective SPF, as would be understood by a person having ordinary skill in the art. For example, the average weight of an amino acid may be about 110 daltons (i.e., 110 g/mol). Therefore, in some embodiments, dividing the molecular weight of a linear protein by

110 daltons may be used to approximate the number of amino acid residues contained therein.

In an embodiment, SPF in a composition of the present disclosure have a polydispersity ranging from 1 to about 5.0, including, without limitation, a polydispersity of 1. In an embodiment, SPF in a composition of the present disclosure have a polydispersity ranging from about 1.5 to about 3.0. In an embodiment, SPF in a composition of the present disclosure have a polydispersity ranging from 1 to about 1.5, including, without limitation, a polydispersity of 1. In an embodiment, SPF in a composition of the present disclosure have a polydispersity ranging from about 1.5 to about 2.0. In an embodiment, SPF in a composition of the present disclosure have a polydispersity ranging from about 2.0 to about 2.5. In an embodiment, SPF in a composition of the present disclosure have a polydispersity ranging from about 2.5 to about 3.0. In an embodiment, SPF in a composition of the present disclosure have a polydispersity ranging from about 3.0 to about 3.5. In an embodiment, SPF in a composition of the present disclosure have a polydispersity ranging from about 3.5 to about 4.0. In an embodiment, SPF in a composition of the present disclosure have a polydispersity ranging from about 4.0 to about 4.5. In an embodiment, SPF in a composition of the present disclosure have a polydispersity ranging from about 4.5 to about 5.0.

In an embodiment, SPF in a composition of the present disclosure have a polydispersity of 1. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 1.1. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 1.2. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 1.3. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 1.4. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 1.5. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 1.6. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 1.7. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 1.8. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of

[illegible]

polydispersity of about 4.5. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 4.6. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 4.7. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 4.8. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 4.9. In an embodiment, SPF in a composition of the present disclosure have a polydispersity of about 5.0.

In some embodiments, in compositions described herein having combinations of low, medium, and/or high molecular weight SPF, such low, medium, and/or high molecular weight SPF may have the same or different polydispersities.

Silk Fibroin Fragments

Methods of making silk fibroin or silk fibroin protein fragments and their applications in various fields are known and are described for example in U.S. Patents Nos. 9,187,538, 9,511,012, 9,517,191, 9,522,107, 9,522,108, 9,545,369, and 10,166,177, 10,287,728 and 10,301,768, all of which are incorporated herein in their entireties. Raw silk from silkworm *Bombyx mori* is composed of two primary proteins: silk fibroin (approximately 75%) and sericin (approximately 25%). Silk fibroin is a fibrous protein with a semi-crystalline structure that provides stiffness and strength. As used herein, the term “silk fibroin” means the fibers of the cocoon of *Bombyx mori* having a weight average molecular weight of about 370,000 Da. The crude silkworm fiber consists of a double thread of fibroin. The adhesive substance holding these double fibers together is sericin. The silk fibroin is composed of a heavy chain having a weight average molecular weight of about 350,000 Da (H chain), and a light chain having a weight average molecular weight about 25,000 Da (L chain). Silk fibroin is an amphiphilic polymer with large hydrophobic domains occupying the major component of the polymer, which has a high molecular weight. The hydrophobic regions are interrupted by small hydrophilic spacers, and the N- and C-termini of the chains are also highly hydrophilic. The hydrophobic domains of the H-chain contain a repetitive hexapeptide sequence of Gly-Ala-Gly-Ala-Gly-Ser and repeats of Gly-Ala/Ser/Tyr dipeptides, which can form stable anti-parallel-sheet crystallites. The amino acid sequence of the L-chain is non-repetitive, so the L-chain is more hydrophilic and relatively elastic. The hydrophilic (Tyr, Ser) and

hydrophobic (Gly, Ala) chain segments in silk fibroin molecules are arranged alternatively such that allows self-assembling of silk fibroin molecules.

Provided herein are methods for producing pure and highly scalable silk fibroin-protein fragment mixture solutions that may be used across multiple industries for a variety of applications. Without wishing to be bound by any particular theory, it is believed that these methods are equally applicable to fragmentation of any SPF described herein, including without limitation recombinant silk proteins, and fragmentation of silk-like or fibroin-like proteins.

As used herein, the term “fibroin” includes silk worm fibroin and insect or spider silk protein. In an embodiment, fibroin is obtained from *Bombyx mori*. Raw silk from *Bombyx mori* is composed of two primary proteins: silk fibroin (approximately 75%) and sericin (approximately 25%). Silk fibroin is a fibrous protein with a semi-crystalline structure that provides stiffness and strength. As used herein, the term “silk fibroin” means the fibers of the cocoon of *Bombyx mori* having a weight average molecular weight of about 370,000 Da. Conversion of these insoluble silk fibroin fibrils into water-soluble silk fibroin protein fragments requires the addition of a concentrated neutral salt (e.g., 8-10 M lithium bromide), which interferes with inter- and intramolecular ionic and hydrogen bonding that would otherwise render the fibroin protein insoluble in water. Methods of making silk fibroin protein fragments, and/or compositions thereof, are known and are described for example in U.S. Patents Nos. 9,187,538, 9,511,012, 9,517,191, 9,522,107, 9,522,108, 9,545,369, and 10,166,177.

The raw silk cocoons from the silkworm *Bombyx mori* was cut into pieces. The pieces silk cocoons were processed in an aqueous solution of Na_2CO_3 at about 100 °C for about 60 minutes to remove sericin (degumming). The volume of the water used equals about 0.4 x raw silk weight and the amount of Na_2CO_3 is about 0.848 x the weight of the raw silk cocoon pieces. The resulting degummed silk cocoon pieces were rinsed with deionized water three times at about 60 °C (20 minutes per rinse). The volume of rinse water for each cycle was 0.2 L x the weight of the raw silk cocoon pieces. The excess water from the degummed silk cocoon pieces was removed. After the DI water washing step, the wet degummed silk cocoon pieces were dried at room temperature. The degummed silk cocoon pieces were mixed with a LiBr solution, and the mixture was

heated to about 100 °C. The warmed mixture was placed in a dry oven and was heated at about 100 °C for about 60 minutes to achieve complete dissolution of the native silk protein. The resulting silk fibroin solution was filtered and dialyzed using Tangential Flow Filtration (TFF) and a 10 kDa membrane against deionized water for 72 hours. The resulting silk fibroin aqueous solution has a concentration of about 8.5 wt. %. Then, 8.5 % silk solution was diluted with water to result in a 1.0 % w/v silk solution. TFF can then be used to further concentrate the pure silk solution to a concentration of 20.0 % w/w silk to water.

Dialyzing the silk through a series of water changes is a manual and time intensive process, which could be accelerated by changing certain parameters, for example diluting the silk solution prior to dialysis. The dialysis process could be scaled for manufacturing by using semi-automated equipment, for example a tangential flow filtration system.

In some embodiments, the silk solutions are prepared under various preparation condition parameters such as: 90 °C 30 min, 90 °C 60 min, 100 °C 30 min, and 100 °C 60 min. Briefly, 9.3 M LiBr was prepared and allowed to sit at room temperature for at least 30 minutes. 5 mL of LiBr solution was added to 1.25 g of silk and placed in the 60 °C oven. Samples from each set were removed at 4, 6, 8, 12, 24, 168 and 192 hours.

In some embodiments, the silk solutions are prepared under various preparation condition parameters such as: 90 °C 30 min, 90 °C 60 min, 100 °C 30 min, and 100 °C 60 min. Briefly, 9.3 M LiBr solution was heated to one of four temperatures: 60 °C, 80 °C, 100 °C or boiling. 5 mL of hot LiBr solution was added to 1.25 g of silk and placed in the 60 °C oven. Samples from each set were removed at 1, 4 and 6 hours.

In some embodiments, the silk solutions are prepared under various preparation condition parameters such as: Four different silk extraction combinations were used: 90 °C 30 min, 90 °C 60 min, 100 °C 30 min, and 100 °C 60 min. Briefly, 9.3 M LiBr solution was heated to one of four temperatures: 60 °C, 80 °C, 100 °C or boiling. 5 mL of hot LiBr solution was added to 1.25 g of silk and placed in the oven at the same temperature of the LiBr. Samples from each set were removed at 1, 4 and 6 hours. 1 mL of each sample was added to 7.5 mL of 9.3 M LiBr and refrigerated for viscosity testing.

In some embodiments, SPF are obtained by dissolving raw unsoured, partially soured, or soured silkworm fibers with a neutral lithium bromide salt. The raw silkworm silks are processed under selected temperature and other conditions in order to remove any sericin and achieve the desired weight average molecular weight (M_w) and polydispersity (PD) of the fragment mixture. Selection of process parameters may be altered to achieve distinct final silk protein fragment characteristics depending upon the intended use. The resulting final fragment solution is silk fibroin protein fragments and water with parts per million (ppm) to non-detectable levels of process contaminants, levels acceptable in the pharmaceutical, medical and consumer eye care markets. The concentration, size and polydispersity of SPF may further be altered depending upon the desired use and performance requirements.

Fig. 18 is a flow chart showing various embodiments for producing pure silk fibroin protein fragments (SPFs) of the present disclosure. It should be understood that not all of the steps illustrated are necessarily required to fabricate all silk solutions of the present disclosure. As illustrated in Fig. 18, step A, cocoons (heat-treated or non-heat-treated), silk fibers, silk powder, spider silk or recombinant spider silk can be used as the silk source. If starting from raw silk cocoons from *Bombyx mori*, the cocoons can be cut into small pieces, for example pieces of approximately equal size, step B1. The raw silk is then extracted and rinsed to remove any sericin, step C1a. This results in substantially sericin free raw silk. In an embodiment, water is heated to a temperature between 84 °C and 100 °C (ideally boiling) and then Na_2CO_3 (sodium carbonate) is added to the boiling water until the Na_2CO_3 is completely dissolved. The raw silk is added to the boiling water/ Na_2CO_3 (100 °C) and submerged for approximately 15 - 90 minutes, where boiling for a longer time results in smaller silk protein fragments. In an embodiment, the water volume equals about 0.4 x raw silk weight and the Na_2CO_3 volume equals about 0.848 x raw silk weight. In an embodiment, the water volume equals 0.1 x raw silk weight and the Na_2CO_3 volume is maintained at 2.12 g/L.

Subsequently, the water dissolved Na_2CO_3 solution is drained and excess water/ Na_2CO_3 is removed from the silk fibroin fibers (e.g., ring out the fibroin extract by hand, spin cycle using a machine, etc.). The resulting silk fibroin extract is rinsed with warm to hot water to remove any remaining adsorbed sericin or contaminate, typically at

a temperature range of about 40 °C to about 80 °C, changing the volume of water at least once (repeated for as many times as required). The resulting silk fibroin extract is a substantially sericin-depleted silk fibroin. In an embodiment, the resulting silk fibroin extract is rinsed with water at a temperature of about 60 °C. In an embodiment, the volume of rinse water for each cycle equals 0.1 L to 0.2 L x raw silk weight. It may be advantageous to agitate, turn or circulate the rinse water to maximize the rinse effect. After rinsing, excess water is removed from the extracted silk fibroin fibers (e.g., ring out fibroin extract by hand or using a machine). Alternatively, methods known to one skilled in the art such as pressure, temperature, or other reagents or combinations thereof may be used for the purpose of sericin extraction. Alternatively, the silk gland (100% sericin free silk protein) can be removed directly from a worm. This would result in liquid silk protein, without any alteration of the protein structure, free of sericin.

The extracted fibroin fibers are then allowed to dry completely. Once dry, the extracted silk fibroin is dissolved using a solvent added to the silk fibroin at a temperature between ambient and boiling, step C1b. In an embodiment, the solvent is a solution of Lithium bromide (LiBr) (boiling for LiBr is 140 °C). Alternatively, the extracted fibroin fibers are not dried but wet and placed in the solvent; solvent concentration can then be varied to achieve similar concentrations as to when adding dried silk to the solvent. The final concentration of LiBr solvent can range from 0.1 M to 9.3 M. Complete dissolution of the extracted fibroin fibers can be achieved by varying the treatment time and temperature along with the concentration of dissolving solvent. Other solvents may be used including, but not limited to, phosphate phosphoric acid, calcium nitrate, calcium chloride solution or other concentrated aqueous solutions of inorganic salts. To ensure complete dissolution, the silk fibers should be fully immersed within the already heated solvent solution and then maintained at a temperature ranging from about 60 °C to about 140 °C for 1-168 hrs. In an embodiment, the silk fibers should be fully immersed within the solvent solution and then placed into a dry oven at a temperature of about 100 °C for about 1 hour.

The temperature at which the silk fibroin extract is added to the LiBr solution (or vice versa) has an effect on the time required to completely dissolve the fibroin and on the resulting molecular weight and polydispersity of the final SPF mixture solution. In an

embodiment, silk solvent solution concentration is less than or equal to 20% w/v. In addition, agitation during introduction or dissolution may be used to facilitate dissolution at varying temperatures and concentrations. The temperature of the LiBr solution will provide control over the silk protein fragment mixture molecular weight and polydispersity created. In an embodiment, a higher temperature will more quickly dissolve the silk offering enhanced process scalability and mass production of silk solution. In an embodiment, using a LiBr solution heated to a temperature between 80 °C - 140 °C reduces the time required in an oven in order to achieve full dissolution. Varying time and temperature at or above 60 °C of the dissolution solvent will alter and control the MW and polydispersity of the SPF mixture solutions formed from the original molecular weight of the native silk fibroin protein.

Alternatively, whole cocoons may be placed directly into a solvent, such as LiBr, bypassing extraction, step B2. This requires subsequent filtration of silk worm particles from the silk and solvent solution and sericin removal using methods known in the art for separating hydrophobic and hydrophilic proteins such as a column separation and/or chromatography, ion exchange, chemical precipitation with salt and/or pH, and/or enzymatic digestion and filtration or extraction, all methods are common examples and without limitation for standard protein separation methods, step C2. Non-heat treated cocoons with the silkworm removed, may alternatively be placed into a solvent such as LiBr, bypassing extraction. The methods described above may be used for sericin separation, with the advantage that non-heat treated cocoons will contain significantly less worm debris.

Dialysis may be used to remove the dissolution solvent from the resulting dissolved fibroin protein fragment solution by dialyzing the solution against a volume of water, step E1. Pre-filtration prior to dialysis is helpful to remove any debris (i.e., silk worm remnants) from the silk and LiBr solution, step D. In one example, a 3 µm or 5 µm filter is used with a flow-rate of 200-300 mL/min to filter a 0.1% to 1.0% silk-LiBr solution prior to dialysis and potential concentration if desired. A method disclosed herein, as described above, is to use time and/or temperature to decrease the concentration from 9.3 M LiBr to a range from 0.1 M to 9.3 M to facilitate filtration and downstream dialysis, particularly when considering creating a scalable process method.

Alternatively, without the use of additional time or temperate, a 9.3 M LiBr-silk protein fragment solution may be diluted with water to facilitate debris filtration and dialysis. The result of dissolution at the desired time and temperate filtration is a translucent particle-free room temperature shelf-stable silk protein fragment-LiBr solution of a known MW and polydispersity. It is advantageous to change the dialysis water regularly until the solvent has been removed (e.g., change water after 1 hour, 4 hours, and then every 12 hours for a total of 6 water changes). The total number of water volume changes may be varied based on the resulting concentration of solvent used for silk protein dissolution and fragmentation. After dialysis, the final silk solution maybe further filtered to remove any remaining debris (i.e., silk worm remnants).

Alternatively, Tangential Flow Filtration (TFF), which is a rapid and efficient method for the separation and purification of biomolecules, may be used to remove the solvent from the resulting dissolved fibroin solution, step E2. TFF offers a highly pure aqueous silk protein fragment solution and enables scalability of the process in order to produce large volumes of the solution in a controlled and repeatable manner. The silk and LiBr solution may be diluted prior to TFF (20% down to 0.1% silk in either water or LiBr). Pre-filtration as described above prior to TFF processing may maintain filter efficiency and potentially avoids the creation of silk gel boundary layers on the filter's surface as the result of the presence of debris particles. Pre-filtration prior to TFF is also helpful to remove any remaining debris (i.e., silk worm remnants) from the silk and LiBr solution that may cause spontaneous or long-term gelation of the resulting water only solution, step D. TFF, recirculating or single pass, may be used for the creation of water-silk protein fragment solutions ranging from 0.1% silk to 30.0% silk (more preferably, 0.1% - 6.0% silk). Different cutoff size TFF membranes may be required based upon the desired concentration, molecular weight and polydispersity of the silk protein fragment mixture in solution. Membranes ranging from 1-100 kDa may be necessary for varying molecular weight silk solutions created for example by varying the length of extraction boil time or the time and temperate in dissolution solvent (e.g., LiBr). In an embodiment, a TFF 5 or 10 kDa membrane is used to purify the silk protein fragment mixture solution and to create the final desired silk-to-water ratio. As well, TFF single pass, TFF, and other methods known in the art, such as a falling film evaporator, may be used to

concentrate the solution following removal of the dissolution solvent (e.g., LiBr) (with resulting desired concentration ranging from 0.1% to 30% silk). This can be used as an alternative to standard HFIP concentration methods known in the art to create a water-based solution. A larger pore membrane could also be utilized to filter out small silk protein fragments and to create a solution of higher molecular weight silk with and/or without tighter polydispersity values.

An assay for LiBr and Na_2CO_3 detection can be performed using an HPLC system equipped with evaporative light scattering detector (ELSD). The calculation was performed by linear regression of the resulting peak areas for the analyte plotted against concentration. More than one sample of a number of formulations of the present disclosure was used for sample preparation and analysis. Generally, four samples of different formulations were weighed directly in a 10 mL volumetric flask. The samples were suspended in 5 mL of 20 mM ammonium formate (pH 3.0) and kept at 2-8 °C for 2 hours with occasional shaking to extract analytes from the film. After 2 hours the solution was diluted with 20 mM ammonium formate (pH 3.0). The sample solution from the volumetric flask was transferred into HPLC vials and injected into the HPLC-ELSD system for the estimation of sodium carbonate and lithium bromide.

The analytical method developed for the quantitation of Na_2CO_3 and LiBr in silk protein formulations was found to be linear in the range 10 - 165 $\mu\text{g/mL}$, with RSD for injection precision as 2% and 1% for area and 0.38% and 0.19% for retention time for sodium carbonate and lithium bromide respectively. The analytical method can be applied for the quantitative determination of sodium carbonate and lithium bromide in silk protein formulations.

Fig. 19 is a flow chart showing various parameters that can be modified during the process of producing a silk protein fragment solution of the present disclosure during the extraction and the dissolution steps. Select method parameters may be altered to achieve distinct final solution characteristics depending upon the intended use, e.g., molecular weight and polydispersity. It should be understood that not all of the steps illustrated are necessarily required to fabricate all silk solutions of the present disclosure.

In an embodiment, silk protein fragment solutions useful for a wide variety of applications are prepared according to the following steps: forming pieces of silk cocoons

from the *Bombyx mori* silkworm; extracting the pieces at about 100 °C in a Na₂CO₃ water solution for about 60 minutes, wherein a volume of the water equals about 0.4 × raw silk weight and the amount of Na₂CO₃ is about 0.848 × the weight of the pieces to form a silk fibroin extract; triple rinsing the silk fibroin extract at about 60 °C for about 20 minutes per rinse in a volume of rinse water, wherein the rinse water for each cycle equals about 0.2 L × the weight of the pieces; removing excess water from the silk fibroin extract; drying the silk fibroin extract; dissolving the dry silk fibroin extract in a LiBr solution, wherein the LiBr solution is first heated to about 100 °C to create a silk and LiBr solution and maintained; placing the silk and LiBr solution in a dry oven at about 100 °C for about 60 minutes to achieve complete dissolution and further fragmentation of the native silk protein structure into mixture with desired molecular weight and polydispersity; filtering the solution to remove any remaining debris from the silkworm; diluting the solution with water to result in a 1.0 wt. % silk solution; and removing solvent from the solution using Tangential Flow Filtration (TFF). In an embodiment, a 10 kDa membrane is utilized to purify the silk solution and create the final desired silk-to-water ratio. TFF can then be used to further concentrate the silk solution to a concentration of 2.0 wt. % silk in water.

Without wishing to be bound by any particular theory, varying extraction (i.e., time and temperature), LiBr (i.e., temperature of LiBr solution when added to silk fibroin extract or vice versa) and dissolution (i.e., time and temperature) parameters results in solvent and silk solutions with different viscosities, homogeneities, and colors. Also without wishing to be bound by any particular theory, increasing the temperature for extraction, lengthening the extraction time, using a higher temperature LiBr solution at emersion and over time when dissolving the silk and increasing the time at temperature (e.g., in an oven as shown here, or an alternative heat source) all resulted in less viscous and more homogeneous solvent and silk solutions.

The extraction step could be completed in a larger vessel, for example an industrial washing machine where temperatures at or in between 60 °C to 100 °C can be maintained. The rinsing step could also be completed in the industrial washing machine, eliminating the manual rinse cycles. Dissolution of the silk in LiBr solution could occur in a vessel other than a convection oven, for example a stirred tank reactor. Dialyzing the silk through a series of water changes is a manual and time intensive process, which

could be accelerated by changing certain parameters, for example diluting the silk solution prior to dialysis. The dialysis process could be scaled for manufacturing by using semi-automated equipment, for example a tangential flow filtration system.

Varying extraction (i.e., time and temperature), LiBr (i.e., temperature of LiBr solution when added to silk fibroin extract or vice versa) and dissolution (i.e., time and temperature) parameters results in solvent and silk solutions with different viscosities, homogeneities, and colors. Increasing the temperature for extraction, lengthening the extraction time, using a higher temperature LiBr solution at emersion and over time when dissolving the silk and increasing the time at temperature (e.g., in an oven as shown here, or an alternative heat source) all resulted in less viscous and more homogeneous solvent and silk solutions. While almost all parameters resulted in a viable silk solution, methods that allow complete dissolution to be achieved in fewer than 4 to 6 hours are preferred for process scalability.

In an embodiment, solutions of silk fibroin protein fragments having a weight average ranging from about 6 kDa to about 17 kDa are prepared according to following steps: degumming a silk source by adding the silk source to a boiling (100 °C) aqueous solution of sodium carbonate for a treatment time of between about 30 minutes to about 60 minutes; removing sericin from the solution to produce a silk fibroin extract comprising non- detectable levels of sericin; draining the solution from the silk fibroin extract; dissolving the silk fibroin extract in a solution of lithium bromide having a starting temperature upon placement of the silk fibroin extract in the lithium bromide solution that ranges from about 60 °C to about 140 °C; maintaining the solution of silk fibroin-lithium bromide in an oven having a temperature of about 140 °C for a period of at most 1 hour; removing the lithium bromide from the silk fibroin extract; and producing an aqueous solution of silk protein fragments, the aqueous solution comprising: fragments having a weight average molecular weight ranging from about 6 kDa to about 17 kDa, and a polydispersity of between 1 and about 5, or between about 1.5 and about 3.0. The method may further comprise drying the silk fibroin extract prior to the dissolving step. The aqueous solution of silk fibroin protein fragments may comprise lithium bromide residuals of less than 300 ppm as measured using a high-performance liquid chromatography lithium bromide assay. The aqueous solution of silk fibroin

protein fragments may comprise sodium carbonate residuals of less than 100 ppm as measured using a high-performance liquid chromatography sodium carbonate assay. The aqueous solution of silk fibroin protein fragments may be lyophilized. In some embodiments, the silk fibroin protein fragment solution may be further processed into various forms including gel, powder, and nanofiber.

In an embodiment, solutions of silk fibroin protein fragments having a weight average molecular weight ranging from about 17 kDa to about 39 kDa are prepared according to the following steps: adding a silk source to a boiling (100 °C) aqueous solution of sodium carbonate for a treatment time of between about 30 minutes to about 60 minutes so as to result in degumming; removing sericin from the solution to produce a silk fibroin extract comprising non-detectable levels of sericin; draining the solution from the silk fibroin extract; dissolving the silk fibroin extract in a solution of lithium bromide having a starting temperature upon placement of the silk fibroin extract in the lithium bromide solution that ranges from about 80 °C to about 140 °C; maintaining the solution of silk fibroin-lithium bromide in a dry oven having a temperature in the range between about 60 °C to about 100 °C for a period of at most 1 hour; removing the lithium bromide from the silk fibroin extract; and producing an aqueous solution of silk fibroin protein fragments, wherein the aqueous solution of silk fibroin protein fragments comprises lithium bromide residuals of between about 10 ppm and about 300 ppm, wherein the aqueous solution of silk protein fragments comprises sodium carbonate residuals of between about 10 ppm and about 100 ppm, wherein the aqueous solution of silk fibroin protein fragments comprises fragments having a weight average molecular weight ranging from about 17 kDa to about 39 kDa, and a polydispersity of between 1 and about 5, or between about 1.5 and about 3.0. The method may further comprise drying the silk fibroin extract prior to the dissolving step. The aqueous solution of silk fibroin protein fragments may comprise lithium bromide residuals of less than 300 ppm as measured using a high- performance liquid chromatography lithium bromide assay. The aqueous solution of silk fibroin protein fragments may comprise sodium carbonate residuals of less than 100 ppm as measured using a high-performance liquid chromatography sodium carbonate assay.

In some embodiments, a method for preparing an aqueous solution of silk fibroin protein fragments having an average weight average molecular weight ranging from about 6 kDa to about 17 kDa includes the steps of: degumming a silk source by adding the silk source to a boiling (100 °C) aqueous solution of sodium carbonate for a treatment time of between about 30 minutes to about 60 minutes; removing sericin from the solution to produce a silk fibroin extract comprising non-detectable levels of sericin; draining the solution from the silk fibroin extract; dissolving the silk fibroin extract in a solution of lithium bromide having a starting temperature upon placement of the silk fibroin extract in the lithium bromide solution that ranges from about 60 °C to about 140 °C; maintaining the solution of silk fibroin-lithium bromide in an oven having a temperature of about 140 °C for a period of at least 1 hour; removing the lithium bromide from the silk fibroin extract; and producing an aqueous solution of silk protein fragments, the aqueous solution comprising: fragments having an average weight average molecular weight ranging from about 6 kDa to about 17 kDa, and a polydispersity of between 1 and about 5, or between about 1.5 and about 3.0. The method may further comprise drying the silk fibroin extract prior to the dissolving step. The aqueous solution of pure silk fibroin protein fragments may comprise lithium bromide residuals of less than 300 ppm as measured using a high-performance liquid chromatography lithium bromide assay . The aqueous solution of pure silk fibroin protein fragments may comprise sodium carbonate residuals of less than 100 ppm as measured using a high-performance liquid chromatography sodium carbonate assay. The method may further comprise adding a therapeutic agent to the aqueous solution of pure silk fibroin protein fragments. The method may further comprise adding a molecule selected from one of an antioxidant or an enzyme to the aqueous solution of pure silk fibroin protein fragments. The method may further comprise adding a vitamin to the aqueous solution of pure silk fibroin protein fragments. The vitamin may be vitamin C or a derivative thereof. The aqueous solution of pure silk fibroin protein fragments may be lyophilized. The method may further comprise adding an alpha hydroxy acid to the aqueous solution of pure silk fibroin protein fragments. The alpha hydroxy acid may be selected from the group consisting of glycolic acid, lactic acid, tartaric acid and citric acid. The method may further comprise adding hyaluronic acid or its salt form at a concentration of about 0.5 % to about 10.0 % to the

aqueous solution of pure silk fibroin protein fragments. The method may further comprise adding at least one of zinc oxide or titanium dioxide. A film may be fabricated from the aqueous solution of pure silk fibroin protein fragments produced by this method. The film may comprise from about 1.0 wt. % to about 50.0 wt. % of vitamin C or a derivative thereof. The film may have a water content ranging from about 2.0 wt. % to about 20.0 wt. %. The film may comprise from about 30.0 wt. % to about 99.5 wt. % of pure silk fibroin protein fragments. A gel may be fabricated from the aqueous solution of pure silk fibroin protein fragments produced by this method. The gel may comprise from about 0.5 wt. % to about 20.0 wt. % of vitamin C or a derivative thereof. The gel may have a silk content of at least 2 % and a vitamin content of at least 20 %.

In some embodiments, a method for preparing an aqueous solution of silk fibroin protein fragments having an average weight average molecular weight ranging from about 17 kDa to about 39 kDa includes the steps of: adding a silk source to a boiling (100 °C) aqueous solution of sodium carbonate for a treatment time of between about 30 minutes to about 60 minutes so as to result in degumming; removing sericin from the solution to produce a silk fibroin extract comprising non-detectable levels of sericin; draining the solution from the silk fibroin extract; dissolving the silk fibroin extract in a solution of lithium bromide having a starting temperature upon placement of the silk fibroin extract in the lithium bromide solution that ranges from about 80 °C to about 140 °C; maintaining the solution of silk fibroin-lithium bromide in a dry oven having a temperature in the range between about 60 °C to about 100 °C for a period of at least 1 hour; removing the lithium bromide from the silk fibroin extract; and producing an aqueous solution of pure silk fibroin protein fragments, wherein the aqueous solution of pure silk fibroin protein fragments comprises lithium bromide residuals of between about 10 ppm and about 300 ppm, wherein the aqueous solution of silk protein fragments comprises sodium carbonate residuals of between about 10 ppm and about 100 ppm, wherein the aqueous solution of pure silk fibroin protein fragments comprises fragments having an average weight average molecular weight ranging from about 17 kDa to about 39 kDa, and a polydispersity of between 1 and about 5, or between about 1.5 and about 3.0. The method may further comprise drying the silk fibroin extract prior to the dissolving step. The aqueous solution of pure silk fibroin protein fragments may

comprise lithium bromide residuals of less than 300 ppm as measured using a high-performance liquid chromatography lithium bromide assay. The aqueous solution of pure silk fibroin protein fragments may comprise sodium carbonate residuals of less than 100 ppm as measured using a high-performance liquid chromatography sodium carbonate assay. The method may further comprise adding a therapeutic agent to the aqueous solution of pure silk fibroin protein fragments. The method may further comprise adding a molecule selected from one of an antioxidant or an enzyme to the aqueous solution of pure silk fibroin protein fragments. The method may further comprise adding a vitamin to the aqueous solution of pure silk fibroin protein fragments. The vitamin may be vitamin C or a derivative thereof. The aqueous solution of pure silk fibroin protein fragments may be lyophilized. The method may further comprise adding an alpha hydroxy acid to the aqueous solution of pure silk fibroin protein fragments. The alpha hydroxy acid may be selected from the group consisting of glycolic acid, lactic acid, tartaric acid and citric acid. The method may further comprise adding hyaluronic acid or its salt form at a concentration of about 0.5% to about 10.0% to the aqueous solution of pure silk fibroin protein fragments. The method may further comprise adding at least one of zinc oxide or titanium dioxide. A film may be fabricated from the aqueous solution of pure silk fibroin protein fragments produced by this method. The film may comprise from about 1.0 wt. % to about 50.0 wt. % of vitamin C or a derivative thereof. The film may have a water content ranging from about 2.0 wt. % to about 20.0 wt. %. The film may comprise from about 30.0 wt. % to about 99.5 wt. % of pure silk fibroin protein fragments. A gel may be fabricated from the aqueous solution of pure silk fibroin protein fragments produced by this method. The gel may comprise from about 0.5 wt. % to about 20.0 wt. % of vitamin C or a derivative thereof. The gel may have a silk content of at least 2% and a vitamin content of at least 20%.

In an embodiment, solutions of silk fibroin protein fragments having a weight average molecular weight ranging from about 39 kDa to about 80 kDa are prepared according to the following steps: adding a silk source to a boiling (100 °C) aqueous solution of sodium carbonate for a treatment time of about 30 minutes so as to result in degumming; removing sericin from the solution to produce a silk fibroin extract comprising non-detectable levels of sericin; draining the solution from the silk fibroin

extract; dissolving the silk fibroin extract in a solution of lithium bromide having a starting temperature upon placement of the silk fibroin extract in the lithium bromide solution that ranges from about 80 °C to about 140 °C; maintaining the solution of silk fibroin-lithium bromide in a dry oven having a temperature in the range between about 60 °C to about 100 °C for a period of at most 1 hour; removing the lithium bromide from the silk fibroin extract; and producing an aqueous solution of silk fibroin protein fragments, wherein the aqueous solution of silk fibroin protein fragments comprises lithium bromide residuals of between about 10 ppm and about 300 ppm, sodium carbonate residuals of between about 10 ppm and about 100 ppm, fragments having a weight average molecular weight ranging from about 39 kDa to about 80 kDa, and a polydispersity of between 1 and about 5, or between about 1.5 and about 3.0. The method may further comprise drying the silk fibroin extract prior to the dissolving step. The aqueous solution of silk fibroin protein fragments may comprise lithium bromide residuals of less than 300 ppm as measured using a high-performance liquid chromatography lithium bromide assay. The aqueous solution of silk fibroin protein fragments may comprise sodium carbonate residuals of less than 100 ppm as measured using a high-performance liquid chromatography sodium carbonate assay. In some embodiments, the method may further comprise adding an active agent (e.g., therapeutic agent) to the aqueous solution of pure silk fibroin protein fragments. The method may further comprise adding an active agent selected from one of an antioxidant or an enzyme to the aqueous solution of pure silk fibroin protein fragments. The method may further comprise adding a vitamin to the aqueous solution of pure silk fibroin protein fragments. The vitamin may be vitamin C or a derivative thereof. The aqueous solution of pure silk fibroin protein fragments may be lyophilized. The method may further comprise adding an alpha-hydroxy acid to the aqueous solution of pure silk fibroin protein fragments. The alpha hydroxy acid may be selected from the group consisting of glycolic acid, lactic acid, tartaric acid and citric acid. The method may further comprise adding hyaluronic acid or its salt form at a concentration of about 0.5% to about 10.0% to the aqueous solution of pure silk fibroin protein fragments. A film may be fabricated from the aqueous solution of pure silk fibroin protein fragments produced by this method. The film may comprise from about 1.0 wt. % to about 50.0 wt. % of vitamin C or a derivative thereof. The film may have a

water content ranging from about 2.0 wt. % to about 20.0 wt. %. The film may comprise from about 30.0 wt. % to about 99.5 wt. % of pure silk fibroin protein fragments. A gel may be fabricated from the aqueous solution of pure silk fibroin protein fragments produced by this method. The gel may comprise from about 0.5 wt. % to about 20.0 wt. % of vitamin C or a derivative thereof. The gel may have a silk content of at least 2 wt. % and a vitamin content of at least 20 wt. %.

Molecular weight of the silk protein fragments may be controlled based upon the specific parameters utilized during the extraction step, including extraction time and temperature; specific parameters utilized during the dissolution step, including the LiBr temperature at the time of submersion of the silk in to the lithium bromide and time that the solution is maintained at specific temperatures; and specific parameters utilized during the filtration step. By controlling process parameters using the disclosed methods, it is possible to create silk fibroin protein fragment solutions with polydispersity equal to or lower than 2.5 at a variety of different molecular weight ranging from 5 kDa to 200 kDa, or between 10 kDa and 80 kDa. By altering process parameters to achieve silk solutions with different molecular weights, a range of fragment mixture end products, with desired polydispersity of equal to or less than 2.5 may be targeted based upon the desired performance requirements. For example, a higher molecular weight silk film containing an ophthalmic drug may have a controlled slow release rate compared to a lower molecular weight film making it ideal for a delivery vehicle in eye care products. Additionally, the silk fibroin protein fragment solutions with a polydispersity of greater than 2.5 can be achieved. Further, two solutions with different average molecular weights and polydispersity can be mixed to create combination solutions. Alternatively, a liquid silk gland (100% sericin free silk protein) that has been removed directly from a worm could be used in combination with any of the silk fibroin protein fragment solutions of the present disclosure. Molecular weight of the pure silk fibroin protein fragment composition was determined using High Pressure Liquid Chromatography (HPLC) with a Refractive Index Detector (RID). Polydispersity was calculated using Cirrus GPC Online GPC/SEC Software Version 3.3 (Agilent).

Differences in the processing parameters can result in regenerated silk fibroins that vary in molecular weight, and peptide chain size distribution (polydispersity, PD).

This, in turn, influences the regenerated silk fibroin performance, including mechanical strength, water solubility etc.

Parameters were varied during the processing of raw silk cocoons into the silk solution. Varying these parameters affected the MW of the resulting silk solution. Parameters manipulated included (i) time and temperature of extraction, (ii) temperature of LiBr, (iii) temperature of dissolution oven, and (iv) dissolution time. Experiments were carried out to determine the effect of varying the extraction time. Tables A-F summarize the results. Below is a summary:

- A sericin extraction time of 30 minutes resulted in larger molecular weight than a sericin extraction time of 60 minutes
- Molecular weight decreases with time in the oven
- 140 °C LiBr and oven resulted in the low end of the confidence interval to be below a molecular weight of 9500 Da
- 30 min extraction at the 1 hour and 4 hour time points have undigested silk
- 30 min extraction at the 1 hour time point resulted in a significantly high molecular weight with the low end of the confidence interval being 35,000 Da
- The range of molecular weight reached for the high end of the confidence interval was 18000 to 216000 Da (important for offering solutions with specified upper limit).

Table A. The effect of extraction time (30 min vs 60 min) on molecular weight of silk processed under the conditions of 100 °C Extraction Temperature, 100 °C Lithium Bromide (LiBr) and 100 °C Oven Dissolution (Oven/Dissolution Time was varied).						
Boil Time	Oven Time	Average Mw	Std dev	Confidence Interval		PD
30	1	57247	12780	35093	93387	1.63
60	1	31520	1387	11633	85407	2.71
30	4	40973	2632	14268	117658	2.87
60	4	25082	1248	10520	59803	2.38
30	6	25604	1405	10252	63943	2.50
60	6	20980	1262	10073	43695	2.08

Table B. The effect of extraction time (30 min vs 60 min) on molecular weight of silk processed under the conditions of 100 °C Extraction Temperature, boiling Lithium Bromide (LiBr) and 60 °C Oven Dissolution for 4 hr.

Sample	Boil Time	Average Mw	Std dev	Confidence Interval		PD
30 min, 4 hr	30	49656	4580	17306	142478	2.87
60 min, 4 hr	60	30042	1536	11183	80705	2.69

Table C. The effect of extraction time (30 min vs 60 min) on molecular weight of silk processed under the conditions of 100 °C Extraction Temperature, 60 °C Lithium Bromide (LiBr) and 60 °C Oven Dissolution (Oven/Dissolution Time was varied).

Sample	Boil Time	Oven Time	Average Mw	Std dev	Confidence Interval		PD
30 min, 1 hr	30	1	58436		22201	153809	2.63
60 min, 1 hr	60	1	31700		11931	84224	2.66
30 min, 4 hr	30	4	61956.5	13337	21463	178847	2.89
60 min, 4 hr	60	4	25578.5	2446	9979	65564	2.56

Table D. The effect of extraction time (30 min vs 60 min) on molecular weight of silk processed under the conditions of 100 °C Extraction Temperature, 80 °C Lithium Bromide (LiBr) and 80 °C Oven Dissolution for 6 hr.

Sample	Boil Time	Average Mw	Std dev	Confidence Interval		PD
30 min, 6 hr	30	63510		18693	215775	3.40
60 min, 6 hr	60	25164	238	9637	65706	2.61

Table E. The effect of extraction time (30 min vs 60 min) on molecular weight of silk processed under the conditions of 100 °C Extraction Temperature, 80 °C Lithium Bromide (LiBr) and 60 °C Oven Dissolution (Oven/Dissolution Time was varied).

Sample	Boil Time	Oven Time	Average Mw	Std dev	Confidence Interval		PD
30 min, 4 hr	30	4	59202	14028	19073	183760	3.10
60 min, 4 hr	60	4	26312.5	637	10266	67442	2.56
30 min, 6 hr	30	6	46824		18076	121293	2.59

60 min, 6 hr	60	6	26353		10168	68302	2.59
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Table F. The effect of extraction time (30 min vs 60 min) on molecular weight of silk processed under the conditions of 100 °C Extraction Temperature, 140 °C Lithium Bromide (LiBr) and 140 °C Oven Dissolution (Oven/Dissolution Time was varied).

Sample	Boil Time	Oven Time	Average Mw	Std dev	Confidence Interval		PD
30 min, 4 hr	30	4	9024.5	1102	4493	18127	2.00865
60 min, 4 hr	60	4	15548		6954	34762	2.2358
30 min, 6 hr	30	6	13021		5987	28319	2.1749
60 min, 6 hr	60	6	10888		5364	22100	2.0298

Experiments were carried out to determine the effect of varying the extraction temperature. **Table G** summarizes the results. Below is a summary:

- Sericin extraction at 90 °C resulted in higher MW than sericin extraction at 100 °C extraction
- Both 90 °C and 100 °C show decreasing MW over time in the oven

Table G. The effect of extraction temperature (90 °C vs. 100 °C) on molecular weight of silk processed under the conditions of 60 min. Extraction Temperature, 100 °C Lithium Bromide (LiBr) and 100 °C Oven Dissolution (Oven/Dissolution Time was varied).

Sample	Boil Time	Oven Time	Average Mw	Std dev	Confidence Interval		PD
90 °C, 4 hr	60	4	37308	4204	13368	104119	2.79
100 °C, 4 hr	60	4	25082	1248	10520	59804	2.38
90 °C, 6 hr	60	6	34224	1135	12717	92100	2.69
100 °C, 6 hr	60	6	20980	1262	10073	43694	2.08

Experiments were carried out to determine the effect of varying the Lithium Bromide (LiBr) temperature when added to silk. **Tables H-I** summarize the results. Below is a summary:

- No impact on molecular weight or confidence interval (all CI ~10500-6500 Da)
- Studies illustrated that the temperature of LiBr-silk dissolution, as LiBr is added and begins dissolving, rapidly drops below the original LiBr temperature due to the majority of the mass being silk at room temperature

Table H. The effect of Lithium Bromide (LiBr) temperature on molecular weight of silk processed under the conditions of 60 min. Extraction Time., 100 °C Extraction Temperature and 60 °C Oven Dissolution (Oven/Dissolution Time was varied).

Sample	LiBr Temp (°C)	Oven Time	Average Mw	Std dev	Confidence Interval		PD
60 °C LiBr, 1 hr	60	1	31700		11931	84223	2.66
100 °C LiBr, 1 hr	100	1	27907	200	10735	72552	2.60
RT LiBr, 4 hr	RT	4	29217	1082	10789	79119	2.71
60 °C LiBr, 4 hr	60	4	25578	2445	9978	65564	2.56
80 °C LiBr, 4 hr	80	4	26312	637	10265	67441	2.56
100 °C LiBr, 4 hr	100	4	27681	1729	11279	67931	2.45
Boil LiBr, 4 hr	Boil	4	30042	1535	11183	80704	2.69
RT LiBr, 6 hr	RT	6	26543	1893	10783	65332	2.46
80 °C LiBr, 6 hr	80	6	26353		10167	68301	2.59
100 °C LiBr, 6 hr	100	6	27150	916	11020	66889	2.46

Table I. The effect of Lithium Bromide (LiBr) temperature on molecular weight of silk processed under the conditions of 30 min. Extraction Time, 100 °C Extraction Temperature and 60 °C Oven Dissolution (Oven/Dissolution Time was varied).

Sample	LiBr Temp (°C)	Oven Time	Average Mw	Std dev	Confidence Interval		PD
60 °C LiBr, 4 hr	60	4	61956	13336	21463	178847	2.89
80 °C LiBr, 4 hr	80	4	59202	14027	19073	183760	3.10
100 °C LiBr, 4 hr	100	4	47853		19757	115899	2.42
80 °C LiBr, 6 hr	80	6	46824		18075	121292	2.59
100 °C LiBr, 6 hr	100	6	55421	8991	19152	160366	2.89

Experiments were carried out to determine the effect of v oven/dissolution temperature. **Tables J-N** summarize the results. Below is a summary:

- Oven temperature has less of an effect on 60 min extracted silk than 30 min extracted silk. Without wishing to be bound by theory, it is believed that the 30 min silk is less degraded during extraction and therefore the oven temperature has more of an effect on the larger MW, less degraded portion of the silk.
- For 60 °C vs. 140 °C oven the 30 min extracted silk showed a very significant effect of lower MW at higher oven temp, while 60 min extracted silk had an effect but much less
- The 140 °C oven resulted in a low end in the confidence interval at ~6000 Da.

Table J. The effect of oven/dissolution temperature on molecular weight of silk processed under the conditions of 100 °C Extraction Temperature, 30 min. Extraction Time, and 100 °C Lithium Bromide (LiBr) (Oven/Dissolution Time was varied).

Boil Time	Oven Temp (°C)	Oven Time	Average Mw	Std dev	Confidence Interval		PD
30	60	4	47853		19758	115900	2.42
30	100	4	40973	2632	14268	117658	2.87
30	60	6	55421	8992	19153	160366	2.89
30	100	6	25604	1405	10252	63943	2.50

Table K. The effect of oven/dissolution temperature on molecular weight of silk processed under the conditions of 100 °C Extraction Temperature, 60 min. Extraction Time, and 100 °C Lithium Bromide (LiBr) (Oven/Dissolution Time was varied).

Boil Time (minutes)	Oven Temp	Oven Time	Average Mw	Std dev	Confidence Interval		PD
60	60	1	27908	200	10735	72552	2.60
60	100	1	31520	1387	11633	85407	2.71
60	60	4	27681	1730	11279	72552	2.62
60	100	4	25082	1248	10520	59803	2.38
60	60	6	27150	916	11020	66889	2.46
60	100	6	20980	1262	10073	43695	2.08

Table L. The effect of oven/dissolution temperature on molecular weight of silk processed under the conditions of 100 °C Extraction Temperature, 60 min. Extraction Time, and 140 °C Lithium Bromide (LiBr) (Oven/Dissolution Time was varied).

Boil Time (minutes)	Oven Temp(°C)	Oven Time	Average	Std dev	Confidence Interval		PD
60	60	4	30042	1536	11183	80705	2.69
60	140	4	15548		7255	33322	2.14

Table M. The effect of oven/dissolution temperature on molecular weight of silk processed under the conditions of 100 °C Extraction Temperature, 30 min. Extraction Time, and 140 °C Lithium Bromide (LiBr) (Oven/Dissolution Time was varied).

Boil Time (minutes)	Oven Temp (°C)	Oven Time	Average Mw	Std dev	Confidence Interval		PD
30	60	4	49656	4580	17306	142478	2.87
30	140	4	9025	1102	4493	18127	2.01
30	60	6	59383	11640	17641	199889	3.37
30	140	6	13021		5987	28319	2.17

Table N. The effect of oven/dissolution temperature on molecular weight of silk processed under the conditions of 100 °C Extraction Temperature, 60 min. Extraction Time, and 80 °C Lithium Bromide (LiBr) (Oven/Dissolution Time was varied).

Boil Time (minutes)	Oven Temp (°C)	Oven Time	Average Mw	Std dev	Confidence Interval		PD
60	60	4	26313	637	10266	67442	2.56
60	80	4	30308	4293	12279	74806	2.47
60	60	6	26353		10168	68302	2.59
60	80	6	25164	238	9637	65706	2.61

The raw silk cocoons from the silkworm *Bombyx mori* was cut into pieces. The pieces of raw silk cocoons were boiled in an aqueous solution of Na₂CO₃ (about 100 °C) for a period of time between about 30 minutes to about 60 minutes to remove sericin (degumming). The volume of the water used equals about 0.4 x raw silk weight and the

amount of Na_2CO_3 is about $0.848 \times$ the weight of the raw silk cocoon pieces. The resulting degummed silk cocoon pieces were rinsed with deionized water three times at about 60°C (20 minutes per rinse). The volume of rinse water for each cycle was $0.2 \text{ L} \times$ the weight of the raw silk cocoon pieces. The excess water from the degummed silk cocoon pieces was removed. After the DI water washing step, the wet degummed silk cocoon pieces were dried at room temperature. The degummed silk cocoon pieces were mixed with a LiBr solution, and the mixture was heated to about 100°C . The warmed mixture was placed in a dry oven and was heated at a temperature ranging from about 60°C to about 140°C for about 60 minutes to achieve complete dissolution of the native silk protein. The resulting solution was allowed to cool to room temperature and then was dialyzed to remove LiBr salts using a 3,500 Da MWCO membrane. Multiple exchanges were performed in DI water until Br^- ions were less than 1 ppm as determined in the hydrolyzed fibroin solution read on an Oakton Bromide (Br^-) double-junction ion-selective electrode.

The resulting silk fibroin aqueous solution has a concentration of about 8.0 % w/v containing pure silk fibroin protein fragments having an average weight average molecular weight ranging from about 6 kDa to about 16 kDa, about 17 kDa to about 39 kDa, and about 39 kDa to about 80 kDa and a polydispersity of between about 1.5 and about 3.0. The 8.0 % w/v was diluted with DI water to provide a 1.0 % w/v, 2.0 % w/v, 3.0 % w/v, 4.0 % w/v, 5.0 % w/v by the coating solution.

A variety of % silk concentrations have been produced through the use of Tangential Flow Filtration (TFF). In all cases a 1 % silk solution was used as the input feed. A range of 750-18,000 mL of 1% silk solution was used as the starting volume. Solution is diafiltered in the TFF to remove lithium bromide. Once below a specified level of residual LiBr, solution undergoes ultrafiltration to increase the concentration through removal of water. See examples below.

Six (6) silk solutions were utilized in standard silk structures with the following results:

Solution #1 is a silk concentration of 5.9 wt. %, average MW of 19.8 kDa and 2.2 PDI (made with a 60 min boil extraction, 100°C LiBr dissolution for 1 hour).

Solution #2 is a silk concentration of 6.4 wt. % (made with a 30 min boil extraction, 60 °C LiBr dissolution for 4 hrs).

Solution #3 is a silk concentration of 6.17 wt. % (made with a 30 min boil extraction 100 °C LiBr dissolution for 1 hour).

Solution #4 is a silk concentration of 7.30 wt. %: A 7.30 % silk solution was produced beginning with 30 minute extraction batches of 100 g silk cocoons per batch. Extracted silk fibers were then dissolved using 100 °C 9.3 M LiBr in a 100 °C oven for 1 hour. 100 g of silk fibers were dissolved per batch to create 20% silk in LiBr. Dissolved silk in LiBr was then diluted to 1% silk and filtered through a 5 µm filter to remove large debris. 15,500 mL of 1 %, filtered silk solution was used as the starting volume/diafiltration volume for TFF. Once LiBr was removed, the solution was ultrafiltered to a volume around 1300 mL. 1262 mL of 7.30 % silk was then collected. Water was added to the feed to help remove the remaining solution and 547 mL of 3.91 % silk was then collected.

Solution #5 is a silk concentration of 6.44 wt. %: A 6.44 wt. % silk solution was produced beginning with 60 minute extraction batches of a mix of 25, 33, 50, 75 and 100 g silk cocoons per batch. Extracted silk fibers were then dissolved using 100 °C 9.3 M LiBr in a 100 °C oven for 1 hour. 35, 42, 50 and 71 g per batch of silk fibers were dissolved to create 20 % silk in LiBr and combined. Dissolved silk in LiBr was then diluted to 1 % silk and filtered through a 5 µm filter to remove large debris. 17,000 mL of 1 %, filtered silk solution was used as the starting volume/diafiltration volume for TFF. Once LiBr was removed, the solution was ultrafiltered to a volume around 3000 mL. 1490 mL of 6.44 % silk was then collected. Water was added to the feed to help remove the remaining solution and 1454 mL of 4.88 % silk was then collected.

Solution #6 is a silk concentration of 2.70 wt. %: A 2.70 % silk solution was produced beginning with 60-minute extraction batches of 25 g silk cocoons per batch. Extracted silk fibers were then dissolved using 100 °C 9.3 M LiBr in a 100 °C oven for 1 hour. 35.48 g of silk fibers were dissolved per batch to create 20 % silk in LiBr. Dissolved silk in LiBr was then diluted to 1% silk and filtered through a 5 µm filter to remove large debris. 1000 mL of 1%, filtered silk solution was used as the starting

volume/diafiltration volume for TFF. Once LiBr was removed, the solution was ultrafiltered to a volume around 300 mL. 312 mL of 2.7 % silk was then collected.

The preparation of silk fibroin solutions with higher molecular weights is given in **Table O**.

Table O. Preparation and properties of silk fibroin solutions.						
Sample Name	Extraction Time (mins)	Extraction Temp (°C)	LiBr Temp (°C)	Oven/Sol'n Temp	Average weight average molecular weight (kDa)	Average polydispersity
Group A TFF	60	100	100	100 °C oven	34.7	2.94
Group A DIS	60	100	100	100 °C oven	44.7	3.17
Group B TFF	60	100	100	100 °C sol'n	41.6	3.07
Group B DIS	60	100	100	100 °C sol'n	44.0	3.12
Group D DIS	30	90	60	60 °C sol'n	129.7	2.56
Group D FIL	30	90	60	60 °C sol'n	144.2	2.73
Group E DIS	15	100	RT	60 °C sol'n	108.8	2.78
Group E FIL	15	100	RT	60 °C sol'n	94.8	2.62

Silk aqueous coating composition for application to fabrics are given in **Tables P and Q** below.

Table P. Silk Solution Characteristics					
	Molecular Weight:	57 kDa			
	Polydispersity:	1.6			
	% Silk	5.0%	3.0%	1.0%	0.5%
Process Parameters					
	Extraction				
	Boil Time:	30 minutes			
	Boil Temperature:	100 °C			
	Rinse Temperature:	60 °C			

	Dissolution				
	LiBr Temperature:	100			
	Oven Temperature:	100 °C			
	Oven Time:	60 minutes			

Table Q. Silk Solution Characteristics					
	Molecular Weight:	25 kDa			
	Polydispersity:	2.4			
	% Silk	5.0%	3.0%	1.0%	0.5%
Process Parameters					
	Extraction				
	Boil Time:	60 minutes			
	Boil Temperature:	100 °C			
	Rinse Temperature:	60 °C			
	Dissolution				
	LiBr Temperature:	100 °C			
	Oven Temperature:	100 °C			
	Oven Time:	60 minutes			

Three (3) silk solutions were utilized in film making with the following results:

Solution #1 is a silk concentration of 5.9 %, average MW of 19.8 kDa and 2.2 PD (made with a 60 min boil extraction, 100 °C LiBr dissolution for 1 hr).

Solution #2 is a silk concentration of 6.4 % (made with a 30 min boil extraction, 60 °C LiBr dissolution for 4 hrs).

Solution #3 is a silk concentration of 6.17 % (made with a 30 min boil extraction, 100 °C LiBr dissolution for 1 hour).

Films were made in accordance with Rockwood et al. (Nature Protocols; Vol. 6; No. 10; published on-line Sep. 22, 2011; doi:10.1038/nprot.2011.379). 4 mL of 1% or 2% (wt/vol) aqueous silk solution was added into 100 mm Petri dish (Volume of silk can be varied for thicker or thinner films and is not critical) and allowed to dry overnight

uncovered. The bottom of a vacuum desiccator was filled with water. Dry films were placed in the desiccator and vacuum applied, allowing the films to water anneal for 4 hours prior to removal from the dish. Films cast from solution #1 did not result in a structurally continuous film; the film was cracked in several pieces. These pieces of film dissolved in water in spite of the water annealing treatment.

Silk solutions of various molecular weights and/or combinations of molecular weights can be optimized for gel applications. The following provides an example of this process but it not intended to be limiting in application or formulation. Three (3) silk solutions were utilized in gel making with the following results:

Solution #1 is a silk concentration of 5.9 %, average MW of 19.8 kDa and 2.2 PD (made with a 60 min boil extraction, 100 °C LiBr dissolution for 1 hr).

Solution #2 is a silk concentration of 6.4 % (made with a 30 min boil extraction, 60 °C LiBr dissolution for 4 hrs).

Solution #3 is a silk concentration of 6.17 % (made with a 30 min boil extraction, 100 °C LiBr dissolution for 1 hour).

“Egel” is an electrogelation process as described in Rockwood of al. Briefly, 10 ml of aqueous silk solution is added to a 50 ml conical tube and a pair of platinum wire electrodes immersed into the silk solution. A 20 volt potential was applied to the platinum electrodes for 5 minutes, the power supply turned off and the gel collected. Solution #1 did not form an EGEL over the 5 minutes of applied electric current.

Solutions #2 and #3 were gelled in accordance with the published horseradish peroxidase (HRP) protocol. Behavior seemed typical of published solutions.

Materials and Methods: the following equipment and material are used in determination of Silk Molecular weight: Agilent 1100 with chemstation software ver. 10.01; Refractive Index Detector (RID); analytical balance; volumetric flasks (1000 mL, 10 mL and 5 mL); HPLC grade water; ACS grade sodium chloride; ACS grade sodium phosphate dibasic heptahydrate; phosphoric acid; dextran MW Standards-Nominal Molecular Weights of 5 kDa, 11.6 kDa, 23.8 kDa, 48.6 kDa, and 148 kDa; 50 mL PET or polypropylene disposable centrifuge tubes; graduated pipettes; amber glass HPLC vials with Teflon caps; Phenomenex PolySep GFC P-4000 column (size: 7.8 mm x 300 mm).

Procedural Steps:

A) Preparation of 1 L Mobile Phase (0.1 M Sodium Chloride solution in 0.0125 M Sodium phosphate buffer)

Take a 250 mL clean and dry beaker, place it on the balance and tare the weight. Add about 3.3509 g of sodium phosphate dibasic heptahydrate to the beaker. Note down the exact weight of sodium phosphate dibasic weighed. Dissolve the weighed sodium phosphate by adding 100 mL of HPLC water into the beaker. Take care not to spill any of the content of the beaker. Transfer the solution carefully into a clean and dry 1000 mL volumetric flask. Rinse the beaker and transfer the rinse into the volumetric flask. Repeat the rinse 4-5 times. In a separate clean and dry 250 mL beaker weigh exactly about 5.8440 g of sodium chloride. Dissolve the weighed sodium chloride in 50 mL of water and transfer the solution to the sodium phosphate solution in the volumetric flask. Rinse the beaker and transfer the rinse into the volumetric flask. Adjust the pH of the solution to 7.0 ± 0.2 with phosphoric acid. Make up the volume in volumetric flask with HPLC water to 1000 mL and shake it vigorously to homogeneously mix the solution. Filter the solution through 0.45 μm polyamide membrane filter. Transfer the solution to a clean and dry solvent bottle and label the bottle. The volume of the solution can be varied to the requirement by correspondingly varying the amount of sodium phosphate dibasic heptahydrate and sodium chloride.

B) Preparation of Dextran Molecular Weight Standard solutions

At least five different molecular weight standards are used for each batch of samples that are run so that the expected value of the sample to be tested is bracketed by the value of the standard used. Label six 20 mL scintillation glass vials respective to the molecular weight standards. Weigh accurately about 5 mg of each of dextran molecular weight standards and record the weights. Dissolve the dextran molecular weight standards in 5 mL of mobile phase to make a 1 mg/mL standard solution.

C) Preparation of Sample solutions

When preparing sample solutions, if there are limitations on how much sample is available, the preparations may be scaled as long as the ratios are maintained. Depending on sample type and silk protein content in sample weigh enough sample in a 50 mL disposable centrifuge tube on an analytical balance to make a 1 mg/mL sample solution for analysis. Dissolve the sample in equivalent volume of mobile phase make a 1 mg/mL

solution. Tightly cap the tubes and mix the samples (in solution). Leave the sample solution for 30 minutes at room temperature. Gently mix the sample solution again for 1 minute and centrifuge at 4000 RPM for 10 minutes.

D) HPLC analysis of the samples

Transfer 1.0 mL of all the standards and sample solutions into individual HPLC vials. Inject the molecular weight standards (one injection each) and each sample in duplicate. Analyze all the standards and sample solutions using the following HPLC conditions:

Column	PolySep GFC P-4000 (7.8 x 300 mm)
Column Temperature	25 °C
Detector	Refractive Index Detector (Temperature @ 35 °C)
Injection Volume	25.0 µL
Mobile Phase	0.1 M Sodium Chloride solution in 0.0125 M sodium phosphate buffer
Flow Rate	1.0 mL/min
Run Time	20.0 min

E) Data analysis and calculations - Calculation of Average Molecular Weight using Cirrus Software

Upload the chromatography data files of the standards and the analytical samples into Cirrus SEC data collection and molecular weight analysis software. Calculate the weight average molecular weight (M_w), number average molecular weight (M_n), peak average molecular weight (M_p), and polydispersity for each injection of the sample.

Spider Silk Fragments

Spider silks are natural polymers that consist of three domains: a repetitive middle core domain that dominates the protein chain, and non-repetitive N-terminal and C-terminal domains. The large core domain is organized in a block copolymer-like arrangement, in which two basic sequences, crystalline [poly(A) or poly(GA)] and less crystalline (GGX or GPGXX) polypeptides alternate. Dragline silk is the protein complex composed of major ampullate dragline silk protein 1 (MaSp1) and major ampullate dragline silk protein 2 (MaSp2). Both silks are approximately 3500 amino acid long. MaSp1 can be found in the fibre core and the periphery, whereas MaSp2 forms clusters in certain core areas. The large central domains of MaSp1 and MaSp2 are organized in block copolymer-like arrangements, in which two basic sequences, crystalline [poly(A)

or poly(GA)] and less crystalline (GGX or GPGXX) polypeptides alternate in core domain. Specific secondary structures have been assigned to poly(A)/(GA), GGX and GPGXX motifs including β -sheet, α -helix and β -spiral respectively. The primary sequence, composition and secondary structural elements of the repetitive core domain are responsible for mechanical properties of spider silks; whereas, non-repetitive N- and C-terminal domains are essential for the storage of liquid silk dope in a lumen and fibre formation in a spinning duct.

The main difference between *MaSp1* and *MaSp2* is the presence of proline (P) residues accounting for 15% of the total amino acid content in *MaSp2*, whereas *MaSp1* is proline-free. By calculating the number of proline residues in *N. clavipes* dragline silk, it is possible to estimate the presence of the two proteins in fibres; 81% *MaSp1* and 19% *MaSp2*. Different spiders have different ratios of *MaSp1* and *MaSp2*. For example, a dragline silk fibre from the orb weaver *Argiope aurantia* contains 41% *MaSp1* and 59% *MaSp2*. Such changes in the ratios of major ampullate silks can dictate the performance of the silk fibre.

At least seven different types of silk proteins are known for one orb-weaver species of spider. Silks differ in primary sequence, physical properties and functions. For example, dragline silks used to build frames, radii and lifelines are known for outstanding mechanical properties including strength, toughness and elasticity. On an equal weight basis, spider silk has a higher toughness than steel and Kevlar. Flageliform silk found in capture spirals has extensibility of up to 500%. Minor ampullate silk, which is found in auxiliary spirals of the orb-web and in prey wrapping, possesses high toughness and strength almost similar to major ampullate silks, but does not supercontract in water.

Spider silks are known for their high tensile strength and toughness. The recombinant silk proteins also confer advantageous properties to cosmetic or dermatological compositions, in particular to be able to improve the hydrating or softening action, good film forming property and low surface density. Diverse and unique biomechanical properties together with biocompatibility and a slow rate of degradation make spider silks excellent candidates as biomaterials for tissue engineering, guided tissue repair and drug delivery, for cosmetic products (e.g. nail and hair strengthener, skin care products), and industrial materials (e.g. nanowires, nanofibers, surface coatings).

In an embodiment, a silk protein may include a polypeptide derived from natural spider silk proteins. The polypeptide is not limited particularly as long as it is derived from natural spider silk proteins, and examples of the polypeptide include natural spider silk proteins and recombinant spider silk proteins such as variants, analogs, derivatives or the like of the natural spider silk proteins. In terms of excellent tenacity, the polypeptide may be derived from major dragline silk proteins produced in major ampullate glands of spiders. Examples of the major dragline silk proteins include major ampullate spidroin MaSp1 and MaSp2 from *Nephila clavipes*, and ADF3 and ADF4 from *Araneus diadematus*, etc. Examples of the polypeptide derived from major dragline silk proteins include variants, analogs, derivatives or the like of the major dragline silk proteins. Further, the polypeptide may be derived from flagelliform silk proteins produced in flagelliform glands of spiders. Examples of the flagelliform silk proteins include flagelliform silk proteins derived from *Nephila clavipes*, etc.

Examples of the polypeptide derived from major dragline silk proteins include a polypeptide containing two or more units of an amino acid sequence represented by the formula 1: REP1-REP2 (1), preferably a polypeptide containing five or more units thereof, and more preferably a polypeptide containing ten or more units thereof. Alternatively, the polypeptide derived from major dragline silk proteins may be a polypeptide that contains units of the amino acid sequence represented by the formula 1: REP1-REP2 (1) and that has, at a C-terminal, an amino acid sequence represented by any of SEQ ID NOS: 1 to 3 of U.S. Patent No. 9,051,453 or an amino acid sequence having a homology of 90% or more with the amino acid sequence represented by any of SEQ ID NOS: 1 to 3 of U.S. Patent No. 9,051,453. In the polypeptide derived from major dragline silk proteins, units of the amino acid sequence represented by the formula 1: REP1-REP2 (1) may be the same or may be different from each other. In the case of producing a recombinant protein using a microbe such as *Escherichia coli* as a host, the molecular weight of the polypeptide derived from major dragline silk proteins is 500 kDa or less, or 300 kDa or less, or 200 kDa or less, in terms of productivity.

In the formula (1), the REP1 indicates polyalanine. In the REP1, the number of alanine residues arranged in succession is preferably 2 or more, more preferably 3 or more, further preferably 4 or more, and particularly preferably 5 or more. Further, in the

REP1, the number of alanine residues arranged in succession is preferably 20 or less, more preferably 16 or less, further preferably 12 or less, and particularly preferably 10 or less. In the formula (1), the REP2 is an amino acid sequence composed of 10 to 200 amino acid residues. The total number of glycine, serine, glutamine and alanine residues contained in the amino acid sequence is 40% or more, preferably 60% or more, and more preferably 70% or more with respect to the total number of amino acid residues contained therein.

In the major dragline silk, the REP1 corresponds to a crystal region in a fiber where a crystal β sheet is formed, and the REP2 corresponds to an amorphous region in a fiber where most of the parts lack regular configurations and that has more flexibility. Further, the [REP1-REP2] corresponds to a repetitious region (repetitive sequence) composed of the crystal region and the amorphous region, which is a characteristic sequence of dragline silk proteins.

Recombinant Silk Fragments

In some embodiments, the recombinant silk protein refers to recombinant spider silk polypeptides, recombinant insect silk polypeptides, or recombinant mussel silk polypeptides. In some embodiments, the recombinant silk protein fragment disclosed herein include recombinant spider silk polypeptides of *Araneidae* or *Araneoids*, or recombinant insect silk polypeptides of *Bombyx mori*. In some embodiments, the recombinant silk protein fragment disclosed herein include recombinant spider silk polypeptides of *Araneidae* or *Araneoids*. In some embodiments, the recombinant silk protein fragment disclosed herein include block copolymer having repetitive units derived from natural spider silk polypeptides of *Araneidae* or *Araneoids*. In some embodiments, the recombinant silk protein fragment disclosed herein include block copolymer having synthetic repetitive units derived from spider silk polypeptides of *Araneidae* or *Araneoids* and non-repetitive units derived from natural repetitive units of spider silk polypeptides of *Araneidae* or *Araneoids*.

Recent advances in genetic engineering have provided a route to produce various types of recombinant silk proteins. Recombinant DNA technology has been used to provide a more practical source of silk proteins. As used herein “recombinant silk

protein” refers to synthetic proteins produced heterologously in prokaryotic or eukaryotic expression systems using genetic engineering methods.

Various methods for synthesizing recombinant silk peptides are known and have been described by Ausubel et al., Current Protocols in Molecular Biology § 8 (John Wiley & Sons 1987, (1990)), incorporated herein by reference. A gram-negative, rod-shaped bacterium *E. coli* is a well-established host for industrial scale production of proteins. Therefore, the majority of recombinant silks have been produced in *E. coli*. *E. coli* which is easy to manipulate, has a short generation time, is relatively low cost and can be scaled up for larger amounts protein production.

The recombinant silk proteins can be produced by transformed prokaryotic or eukaryotic systems containing the cDNA coding for a silk protein, for a fragment of this protein or for an analog of such a protein. The recombinant DNA approach enables the production of recombinant silks with programmed sequences, secondary structures, architectures and precise molecular weight. There are four main steps in the process: (i) design and assembly of synthetic silk-like genes into genetic ‘cassettes’, (ii) insertion of this segment into a DNA recombinant vector, (iii) transformation of this recombinant DNA molecule into a host cell and (iv) expression and purification of the selected clones.

The term “recombinant vectors”, as used herein, includes any vectors known to the skilled person including plasmid vectors, cosmid vectors, phage vectors such as lambda phage, viral vectors such as adenoviral or baculoviral vectors, or artificial chromosome vectors such as bacterial artificial chromosomes (BAC), yeast artificial chromosomes (YAC), or P1 artificial chromosomes (PAC). Said vectors include expression as well as cloning vectors. Expression vectors comprise plasmids as well as viral vectors and generally contain a desired coding sequence and appropriate DNA sequences necessary for the expression of the operably linked coding sequence in a particular host organism (e.g., bacteria, yeast, or plant) or in in vitro expression systems. Cloning vectors are generally used to engineer and amplify a certain desired DNA fragment and may lack functional sequences needed for expression of the desired DNA fragments.

The prokaryotic systems include Gram-negative bacteria or Gram-positive bacteria. The prokaryotic expression vectors can include an origin of replication which

can be recognized by the host organism, a homologous or heterologous promoter which is functional in the said host, the DNA sequence coding for the spider silk protein, for a fragment of this protein or for an analogous protein. Nonlimiting examples of prokaryotic expression organisms are *Escherichia coli*, *Bacillus subtilis*, *Bacillus megaterium*, *Corynebacterium glutamicum*, *Anabaena*, *Caulobacter*, *Gluconobacter*, *Rhodobacter*, *Pseudomonas*, *Para coccus*, *Bacillus* (e.g. *Bacillus subtilis*) *Brevibacterium*, *Corynebacterium*, *Rhizobium* (*Sinorhizobium*), *Flavobacterium*, *Klebsiella*, *Enterobacter*, *Lactobacillus*, *Lactococcus*, *Methylobacterium*, *Propionibacterium*, *Staphylococcus* or *Streptomyces* cells.

The eukaryotic systems include yeasts and insect, mammalian or plant cells. In this case, the expression vectors can include a yeast plasmid origin of replication or an autonomous replication sequence, a promoter, a DNA sequence coding for a spider silk protein, for a fragment or for an analogous protein, a polyadenylation sequence, a transcription termination site and, lastly, a selection gene. Nonlimiting examples of eukaryotic expression organisms include yeasts, such as *Saccharomyces cerevisiae*, *Pichia pastoris*, *basidiosporogenous*, *ascosporogenous*, filamentous fungi, such as *Aspergillus niger*, *Aspergillus oryzae*, *Aspergillus nidulans*, *Trichoderma reesei*, *Acremonium chrysogenum*, *Candida*, *Hansenula*, *Kluyveromyces*, *Saccharomyces* (e.g. *Saccharomyces cerevisiae*), *Schizosaccharomyces*, *Pichia* (e.g. *Pichia pastoris*) or *Yarrowia* cells etc., mammalian cells, such as HeLa cells, COS cells, CHO cells etc., insect cells, such as Sf9 cells, MEL cells, etc., “insect host cells” such as *Spodoptera frugiperda* or *Trichoplusia ni* cells. *SF9 cells*, *SF-21 cells* or *High-Five cells*, wherein SF-9 and SF-21 are ovarian cells from *Spodoptera frugiperda*, and High-Five cells are egg cells from *Trichoplusia ni*., “plant host cells”, such as tobacco, potato or pea cells.

A variety of heterologous host systems have been explored to produce different types of recombinant silks. Recombinant partial spidroins as well as engineered silks have been cloned and expressed in bacteria (*Escherichia coli*), yeast (*Pichia pastoris*), insects (*silkworm larvae*), plants (tobacco, soybean, potato, *Arabidopsis*), mammalian cell lines (BHT/hamster) and transgenic animals (mice, goats). Most of the silk proteins are produced with an N- or C-terminal His-tags to make purification simple and produce enough amounts of the protein.

In some embodiments, the host suitable for expressing the recombinant spider silk protein using heterogeneous system may include transgenic animals and plants. In some embodiments, the host suitable for expressing the recombinant spider silk protein using heterogeneous system comprises bacteria, yeasts, mammalian cell lines. In some embodiments, the host suitable for expressing the recombinant spider silk protein using heterogeneous system comprises *E. coli*. In some embodiments, the host suitable for expressing the recombinant spider silk protein using heterogeneous system comprises transgenic *B. mori* silkworm generated using genome editing technologies (e.g. CRISPR).

The recombinant silk protein in this disclosure comprises synthetic proteins which are based on repeat units of natural silk proteins. Besides the synthetic repetitive silk protein sequences, these can additionally comprise one or more natural nonrepetitive silk protein sequences.

In some embodiments, “recombinant silk protein” refers to recombinant silkworm silk protein or fragments thereof. The recombinant production of silk fibroin and silk sericin has been reported. A variety of hosts are used for the production including *E. coli*, *Saccharomyces cerevisiae*, *Pseudomonas sp.*, *Rhodopseudomonas sp.*, *Bacillus sp.*, and *Streptomyces*. See EP 0230702, which is incorporated by reference herein by its entirety.

Provided herein also include design and biological-synthesis of silk fibroin protein-like multiblock polymer comprising GAGAGX hexapeptide (X is A, Y, V or S) derived from the repetitive domain of *B. mori* silk heavy chain (H chain)

In some embodiments, this disclosure provides silk protein-like multiblock polymers derived from the repetitive domain of *B. mori* silk heavy chain (H chain) comprising the GAGAGS hexapeptide repeating units. The GAGAGS hexapeptide is the core unit of H-chain and plays an important role in the formation of crystalline domains. The silk protein-like multiblock polymers containing the GAGAGS hexapeptide repeating units spontaneously aggregate into β -sheet structures, similar to natural silk fibroin protein, where in the silk protein-like multiblock polymers having any weight average molecular weight described herein.

In some embodiments, this disclosure provides silk-peptide like multiblock copolymers composed of the GAGAGS hexapeptide repetitive fragment derived from H chain of *B. mori* silk heavy chain and mammalian elastin VPGVG motif produced by *E.*

coli. In some embodiments, this disclosure provides fusion silk fibroin proteins composed of the GAGAGS hexapeptide repetitive fragment derived from H chain of *B. mori* silk heavy chain and GVGVP produced by *E. coli*, where in the silk protein-like multiblock polymers having any weight average molecular weight described herein.

In some embodiments, this disclosure provides *B. mori* silkworm recombinant proteins composed of the (GAGAGS)₁₆ repetitive fragment. In some embodiments, this disclosure provides recombinant proteins composed of the (GAGAGS)₁₆ repetitive fragment and the non-repetitive (GAGAGS)₁₆ –F-COOH, (GAGAGS)₁₆ –F-F-COOH, (GAGAGS)₁₆ –F-F-F-COOH, (GAGAGS)₁₆ –F-F-F-F-COOH, (GAGAGS)₁₆ –F-F-F-F-F-COOH, (GAGAGS)₁₆ –F-F-F-F-F-F-F-F-F-F-COOH produced by *E. coli*, where F has the following amino acid sequence SGFGPVANGGSGEASSEDFGSSGFGPVANASSGEASSEDFAG, and where in the silk protein-like multiblock polymers having any weight average molecular weight described herein.

In some embodiments, “recombinant silk protein” refers to recombinant spider silk protein or fragments thereof. The productions of recombinant spider silk proteins based on a partial cDNA clone have been reported. The recombinant spider silk proteins produced as such comprise a portion of the repetitive sequence derived from a dragline spider silk protein, *Spidroin 1*, from the spider *Nephila clavipes*. see Xu et al. (Proc. Natl. Acad. Sci. U.S.A., 87:7120–7124 (1990). cDNA clone encoding a portion of the repeating sequence of a second fibroin protein, *Spidroin 2*, from dragline silk of *Nephila clavipes* and the recombinant synthesis thereof is described in *J. Biol. Chem.*, 1992, volume 267, pp. 19320–19324. The recombinant synthesis of spider silk proteins including protein fragments and variants of *Nephila clavipes* from transformed *E. coli* is described in U.S. Pat. Nos. 5,728,810 and 5,989,894. cDNA clones encoding minor ampullate spider silk proteins and the expression thereof is described in U.S. Pat. Nos. 5,733,771 and 5,756,677. cDNA clone encoding the flagelliform silk protein from an orb-web spinning spider is described in U.S. Pat. No. 5,994,099. U.S. Pat. No. 6,268,169 describes the recombinant synthesis of spider silk like proteins derived from the repeating peptide sequence found in the natural spider dragline of *Nephila clavipes* by *E. coli*, *Bacillus subtilis*, and *Pichia pastoris* recombinant expression systems. WO 03/020916

describes the cDNA clone encoding and recombinant production of spider spider silk proteins having repetitive sequences derived from the major ampullate glands of *Nephila madagascariensis*, *Nephila senegalensis*, *Tetragnatha kauaiensis*, *Tetragnatha versicolor*, *Argiope aurantia*, *Argiope trifasciata*, *Gasteracantha mammosa*, and *Latrodectus geometricus*, the flagelliform glands of *Argiope trifasciata*, the ampullate glands of *Dolomedes tenebrosus*, two sets of silk glands from *Plectreurys tristis*, and the silk glands of the mygalomorph *Euagrus chioseus*. Each of the above reference is incorporated herein by reference in its entirety.

In some embodiments, the recombinant spider silk protein is a hybrid protein of a spider silk protein and an insect silk protein, a spider silk protein and collagen, a spider silk protein and resilin, or a spider silk protein and keratin. The spider silk repetitive unit comprises or consists of an amino acid sequence of a region that comprises or consists of at least one peptide motif that repetitively occurs within a naturally occurring major ampullate gland polypeptide, such as a dragline spider silk polypeptide, a minor ampullate gland polypeptide, a flagelliform polypeptide, an aggregate spider silk polypeptide, an acini-form spider silk polypeptide or a pyriform spider silk polypeptide.

In some embodiments, the recombinant spider silk protein in this disclosure comprises synthetic spider silk proteins derived from repetitive units of natural spider silk proteins, consensus sequence, and optionally one or more natural non-repetitive spider silk protein sequences. The repeated units of natural spider silk polypeptide may include dragline spider silk polypeptides or flagelliform spider silk polypeptides of *Araneidae* or *Araneoids*.

As used herein, the spider silk “repetitive unit” comprises or consists of at least one peptide motif that repetitively occurs within a naturally occurring major ampullate gland polypeptide, such as a dragline spider silk polypeptide, a minor ampullate gland polypeptide, a flagelliform polypeptide, an aggregate spider silk polypeptide, an acini-form spider silk polypeptide or a pyriform spider silk polypeptide. A “repetitive unit” refers to a region which corresponds in amino acid sequence to a region that comprises or consists of at least one peptide motif (e.g. AAAAAA) or GPGQQ) that repetitively occurs within a naturally occurring silk polypeptide (e.g. MaSpI, ADF-3, ADF-4, or Flag) (i.e. identical amino acid sequence) or to an amino acid sequence

substantially similar thereto (i.e. variational amino acid sequence). A “repetitive unit” having an amino acid sequence which is “substantially similar” to a corresponding amino acid sequence within a naturally occurring silk polypeptide (i.e. wild-type repetitive unit) is also similar with respect to its properties, e.g. a silk protein comprising the “substantially similar repetitive unit” is still insoluble and retains its insolubility. A “repetitive unit” having an amino acid sequence which is “identical” to the amino acid sequence of a naturally occurring silk polypeptide, for example, can be a portion of a silk polypeptide corresponding to one or more peptide motifs of MaSpI, MaSpII, ADF-3 and/or ADF-4. A “repetitive unit” having an amino acid sequence which is “substantially similar” to the amino acid sequence of a naturally occurring silk polypeptide, for example, can be a portion of a silk polypeptide corresponding to one or more peptide motifs of MaSpI, MaSpII, ADF-3 and/or ADF-4, but having one or more amino acid substitution at specific amino acid positions.

As used herein, the term “consensus peptide sequence” refers to an amino acid sequence which contains amino acids which frequently occur in a certain position (e.g. “G”) and wherein, other amino acids which are not further determined are replaced by the place holder “X”. In some embodiments, the consensus sequence is at least one of (i) GPGXX, wherein X is an amino acid selected from A, S, G, Y, P and Q; (ii) GGX, wherein X is an amino acid selected from Y, P, R, S, A, T, N and Q, preferably Y, P and Q; (iii) A_x, wherein x is an integer from 5 to 10.

The consensus peptide sequences GPGXX and GGX, i.e. glycine rich motifs, provide flexibility to the silk polypeptide and thus, to the thread formed from the silk protein containing said motifs. In detail, the iterated GPGXX motif forms turn spiral structures, which imparts elasticity to the silk polypeptide. Major ampullate and flagelliform silks both have a GPGXX motif. The iterated GGX motif is associated with a helical structure having three amino acids per turn and is found in most spider silks. The GGX motif may provide additional elastic properties to the silk. The iterated polyalanine A_x (peptide) motif forms a crystalline β -sheet structure that provides strength to the silk polypeptide, as described for example in WO 03/057727.

In some embodiments, the recombinant spider silk protein in this disclosure comprises two identical repetitive units each comprising at least one, preferably one,

amino acid sequence selected from the group consisting of: GGRPSDTYG and GGRPSSSYG derived from Resilin. Resilin is an elastomeric protein found in most arthropods that provides low stiffness and high strength.

As used herein, “non-repetitive units” refers to an amino acid sequence which is “substantially similar” to a corresponding non-repetitive (carboxy terminal) amino acid sequence within a naturally occurring dragline polypeptide (i.e. wild-type non-repetitive (carboxy terminal) unit), preferably within ADF-3 (SEQ ID NO:1), ADF-4 (SEQ ID NO:2), NR3 (SEQ ID NO:41), NR4 (SEQ ID NO:42), ADF-4 of the spider *Araneus diadematus* as described in U.S. Pat. No. 8,367,803, C16 peptide (spider silk protein eADF4, molecular weight of 47.7 kDa, AMSilk) comprising the 16 repeats of the sequence GSSAAAAAASGPGGYGPENQGPGSGPGGYGPGGP, an amino acid sequence adapted from the natural sequence of ADF4 from *A. diadematus*. Non-repetitive ADF-4 and variants thereof display efficient assembly behavior.

Among the synthetic spider silk proteins, the recombinant silk protein in this disclosure comprises in some embodiments the C16-protein having the polypeptide sequence SEQ ID NO: 1 as described in U.S. Patent No. 8288512. Besides the polypeptide sequence shown in SEQ ID NO:1, particularly functional equivalents, functional derivatives and salts of this sequence are also included.

As used herein, “functional equivalents” refers to mutant which, in at least one sequence position of the abovementioned amino acid sequences, have an amino acid other than that specifically mentioned.

In some embodiments, the recombinant spider silk protein in this disclosure comprises, in an effective amount, at least one natural or recombinant silk protein including spider silk protein, corresponding to Spidroin major 1 described by Xu et al., PNAS, USA, 87, 7120, (1990), Spidroin major 2 described by Hinman and Lewis, J. Biol. Chem., 267, 19320, (1992), recombinant spider silk protein as described in U.S. Patent Application No. 2016/0222174 and U.S. Patent Nos. 9,051,453, 9,617,315, 9,689,089, 8,173,772, 8,642,734, 8,367,803 8,097,583, 8,030,024, 7,754,851, 7,148,039, 7,060,260, or alternatively the minor Spidroins described in patent application WO 95/25165. Each of the above-cited references is incorporated herein by reference in its entirety. Additional recombinant spider silk proteins suitable for the recombinant RSPF

of this disclosure include ADF3 and ADF4 from the “Major Ampullate” gland of *Araneus diadematus*.

Recombinant silk is also described in other patents and patent applications, incorporated by reference herein: US 2004590196, US 7,754,851, US 2007654470, US 7,951,908, US 2010785960, US 8,034,897, US 20090263430, US 2008226854, US 20090123967, US 2005712095, US 2007991037, US 20090162896, US 200885266, US 8,372,436, US 2007989907, US 2009267596, US 2010319542, US 2009265344, US 2012684607, US 2004583227, US 8,030,024, US 2006643569, US 7,868,146, US 2007991916, US 8,097,583, US 2006643200, US 8,729,238, US 8,877,903, US 20190062557, US 20160280960, US 20110201783, US 2008991916, US 2011986662, US 2012697729, US 20150328363, US 9,034,816, US 20130172478, US 9,217,017, US 20170202995, US 8,721,991, US 2008227498, US 9,233,067, US 8,288,512, US 2008161364, US 7,148,039, US 1999247806, US 2001861597, US 2004887100, US 9,481,719, US 8,765,688, US 200880705, US 2010809102, US 8,367,803, US 2010664902, US 7,569,660, US 1999138833, US 2000591632, US 20120065126, US 20100278882, US 2008161352, US 20100015070, US 2009513709, US 20090194317, US 2004559286, US 200589551, US 2008187824, US 20050266242, US 20050227322, and US 20044418.

Recombinant silk is also described in other patents and patent applications, incorporated by reference herein: US 20190062557, US 20150284565, US 20130225476, US 20130172478, US 20130136779, US 20130109762, US 20120252294, US 20110230911, US 20110201783, US 20100298877, US 10,478,520, US 10,253,213, US 10,072,152, US 9,233,067, US 9,217,017, US 9,034,816, US 8,877,903, US 8,729,238, US 8,721,991, US 8,097,583, US 8,034,897, US 8,030,024, US 7,951,908, US 7,868,146, and US 7,754,851.

In some embodiments, the recombinant spider silk protein in this disclosure comprises or consists of 2 to 80 repetitive units, each independently selected from GPGXX, GGX and A_x as defined herein.

In some embodiments, the recombinant spider silk protein in this disclosure comprises or consists of repetitive units each independently selected from selected from the group consisting of GPGAS, GPGSG, GPGGY, GPGGP, GPGGA, GPGQQ,

GPGGG, GPGQG, GPGGS, GGY, GGP, GGA, GGR, GGS, GGT, GGN, GGQ, AAAAA, AAAAA, AAAAA, AAAAA, AAAAA, AAAAA, AAAAA, AAAAA, GGRPSDTYG and GGRPSSSYG, (i) GPYGPASAAAAAGGYGPGSGQQ, (ii) GSSAAAAAASGPGGYGPENQGPSGPGGYGPGGP, (iii) GPGQQGPGQQGPGQQGPGQQ: (iv) GPGGAGGPYGPAGGAGGPYGPAGGAGGPY, (v) GGTTIIEDLDITIDGADGPITISEELTI, (vi) PGSSAAAAAASGPGQGQGQGQGQGGRPSDTYG, (vii) SAAAAAAGPGGGNGGRPSDTYGAPGGGNGGRPSSSYG, (viii) GGAGGAGGAGGSGGAGGS (SEQ ID NO: 27), (ix) GPGGAGPGGYGPGGSGPGGYGPGGSGPGGY, (x) GPYGPASAAAAAGGYGPGCGQQ, (xi) GPYGPASAAAAAGGYGPGKGQQ, (xii) GSSAAAAAASGPGGYGPENQGPCGPGGYGPGGP, (xiii) GSSAAAAAASGPGGYGPKNQGPSGPGGYGPGGP, (xiv) GSSAAAAAASGPGGYGPKNQGPSGPGGYGPGGP, or variants thereof as described in U.S. Pat. No. 8,877,903, for example, a synthetic spider peptide having sequential order of GPGAS, GGY, GPGSG in the peptide chain, or sequential order of AAAAAA, GPGGY, GPGGP in the peptide chain, sequential order of AAAAAA, GPGQG, GGR in the peptide chain.

In some embodiments, this disclosure provides silk protein-like multiblock peptides that imitate the repeating units of amino acids derived from natural spider silk proteins such as *Spidroin major* 1 domain, *Spidroin major* 2 domain or *Spidroin minor* 1 domain and the profile of variation between the repeating units without modifying their three-dimensional conformation, wherein these silk protein-like multiblock peptides comprise a repeating unit of amino acids corresponding to one of the sequences (I), (II), (III) and/or (IV) below.

$[(XGG)_w(XGA)(GXG)_x(AGA)_y(G)_zAG]_p$ Formula (I) in which: X corresponds to tyrosine or to glutamine, w is an integer equal to 2 or 3, x is an integer from 1 to 3, y is an integer from 5 to 7, z is an integer equal to 1 or 2, and p is an integer and having any weight average molecular weight described herein, and/or

$[(\text{GPG}_2\text{YGPGQ}_2)_a(\text{X}')_2\text{S(A)}_b]_p$ Formula (II) in which: X' corresponds to the amino acid sequence GPS or GPG, a is equal to 2 or 3, b is an integer from 7 to 10, and p is an integer and having any weight average molecular weight described herein, and/or

$[(\text{GR})(\text{GA})_l(\text{A})_m(\text{GGX})_n(\text{GA})_l(\text{A})_m]_p$ Formula (III) and/or $[(\text{GGX})_n(\text{GA})_m(\text{A})_l]_p$ Formula (IV) in which: X'' corresponds to tyrosine, glutamine or alanine, l is an integer from 1 to 6, m is an integer from 0 to 4, n is an integer from 1 to 4, and p is an integer.

In some embodiments, the recombinant spider silk protein or an analog of a spider silk protein comprising an amino acid repeating unit of sequence (V):

$[(\text{Xaa Gly Gly})_w(\text{Xaa Gly Ala})(\text{Gly Xaa Gly})_x(\text{Ala Gly Ala})_y(\text{Gly})_z\text{Ala Gly}]_p$ Formula (V), wherein Xaa is tyrosine or glutamine, w is an integer equal to 2 or 3, x is an integer from 1 to 3, y is an integer from 5 to 7, z is an integer equal to 1 or 2, and p is an integer.

In some embodiments, the recombinant spider silk protein in this disclosure is selected from the group consisting of ADF-3 or variants thereof, ADF-4 or variants thereof, MaSpI (SEQ ID NO: 43) or variants thereof, MaSpII (SEQ ID NO: 44) or variants thereof as described in U.S. Pat. No. 8,367,803.

In some embodiments, this disclosure provides water soluble recombinant spider silk proteins produced in mammalian cells. The solubility of the spider silk proteins produced in mammalian cells was attributed to the presence of the COOH-terminus in these proteins, which makes them more hydrophilic. These COOH-terminal amino acids are absent in spider silk proteins expressed in microbial hosts.

In some embodiments, the recombinant spider silk protein in this disclosure comprises water soluble recombinant spider silk protein C16 modified with an amino or carboxyl terminal selected from the amino acid sequences consisting of: GCGGGGGG, GKGGGGGG, GCGGSGGGGSGGGG, GKGGGGGGSGGGG, and GCGGGGGGSGGGG. In some embodiments, the recombinant spider silk protein in this disclosure comprises C₁₆NR₄, C₃₂NR₄, C16, C32, NR₄C₁₆NR₄, NR₄C₃₂NR₄, NR₃C₁₆NR₃, or NR₃C₃₂NR₃ such that the molecular weight of the protein ranges as described herein.

In some embodiments, the recombinant spider silk protein in this disclosure comprises recombinant spider silk protein having a synthetic repetitive peptide segments

and an amino acid sequence adapted from the natural sequence of ADF4 from *A. diadematus* as described in U.S. Pat. No. 8,877,903. In some embodiments, the RSPF in this disclosure comprises the recombinant spider silk proteins having repeating peptide units derived from natural spider silk proteins such as *Spidroin major* 1 domain, *Spidroin major* 2 domain or *Spidroin minor* 1 domain, wherein the repeating peptide sequence is GSSAAAAAAAAASGPGQGQGQGQGGRPSDTYG or SAAAAAAAAAGPGGGNGGRPSDTYGAPGGGNGGRPSSSYG, as described in U.S. Pat. No. 8,367,803.

In some embodiments, this disclosure provides recombinant spider proteins composed of the GPGGAGPGGYGPGGSGPGGYGPGGSGPGGY repetitive fragment and having a molecular weight as described herein.

As used herein, the term “recombinant silk” refers to recombinant spider and/or silkworm silk protein or fragments thereof. In an embodiment, the spider silk protein is selected from the group consisting of swathing silk (Achniform gland silk), egg sac silk (Cylindriform gland silk), egg case silk (Tubuliform silk), non-sticky dragline silk (Ampullate gland silk), attaching thread silk (Pyriform gland silk), sticky silk core fibers (Flagelliform gland silk), and sticky silk outer fibers (Aggregate gland silk). For example, recombinant spider silk protein, as described herein, includes the proteins described in U.S. Patent Application No. 2016/0222174 and U.S. Patent Nos. 9,051,453, 9,617,315, 9,689,089, 8,173,772, and 8,642,734.

Some organisms make multiple silk fibers with unique sequences, structural elements, and mechanical properties. For example, orb weaving spiders have six unique types of glands that produce different silk polypeptide sequences that are polymerized into fibers tailored to fit an environmental or lifecycle niche. The fibers are named for the gland they originate from and the polypeptides are labeled with the gland abbreviation (e.g. “Ma”) and “Sp” for spidroin (short for spider fibroin). In orb weavers, these types include Major Ampullate (MaSp, also called dragline), Minor Ampullate (MiSp), Flagelliform (Flag), Aciniform (AcSp), Tubuliform (TuSp), and Pyriform (PySp). This combination of polypeptide sequences across fiber types, domains, and variation amongst different genus and species of organisms leads to a vast array of potential properties that can be harnessed by commercial production of the recombinant fibers. To date, the vast

majority of the work with recombinant silks has focused on the Major Ampullate Spidroins (MaSp).

Aciniform (AcSp) silks tend to have high toughness, a result of moderately high strength coupled with moderately high extensibility. AcSp silks are characterized by large block (“ensemble repeat”) sizes that often incorporate motifs of poly serine and GPX. Tubuliform (TuSp or Cylindrical) silks tend to have large diameters, with modest strength and high extensibility. TuSp silks are characterized by their poly serine and poly threonine content, and short tracts of poly alanine. Major Ampullate (MaSp) silks tend to have high strength and modest extensibility. MaSp silks can be one of two subtypes: MaSp1 and MaSp2. MaSp1 silks are generally less extensible than MaSp2 silks, and are characterized by poly alanine, GX, and GGX motifs. MaSp2 silks are characterized by poly alanine, GGX, and GPX motifs. Minor Ampullate (MiSp) silks tend to have modest strength and modest extensibility. MiSp silks are characterized by GGX, GA, and poly A motifs, and often contain spacer elements of approximately 100 amino acids. Flagelliform (Flag) silks tend to have very high extensibility and modest strength. Flag silks are usually characterized by GPG, GGX, and short spacer motifs.

Silk polypeptides are characteristically composed of a repeat domain (REP) flanked by non-repetitive regions (e.g., C-terminal and N-terminal domains). In an embodiment, both the C-terminal and N-terminal domains are between 75-350 amino acids in length. The repeat domain exhibits a hierarchical architecture. The repeat domain comprises a series of blocks (also called repeat units). The blocks are repeated, sometimes perfectly and sometimes imperfectly (making up a quasi-repeat domain), throughout the silk repeat domain. The length and composition of blocks varies among different silk types and across different species. Table 1 of U.S. Published Application No. 2016/0222174, the entirety of which is incorporated herein, lists examples of block sequences from selected species and silk types, with further examples presented in Rising, A. et al., Spider silk proteins: recent advances in recombinant production, structure-function relationships and biomedical applications, *Cell Mol. Life Sci.*, 68:2, pg 169-184 (2011); and Gatesy, J. et al., Extreme diversity, conservation, and convergence of spider silk fibroin sequences, *Science*, 291:5513, pg. 2603-2605 (2001). In some cases, blocks may be arranged in a regular pattern, forming larger macro-repeats that appear

multiple times (usually 2-8) in the repeat domain of the silk sequence. Repeated blocks inside a repeat domain or macro-repeat, and repeated macro-repeats within the repeat domain, may be separated by spacing elements.

The construction of certain spider silk block copolymer polypeptides from the blocks and/or macro-repeat domains, according to certain embodiments of the disclosure, is illustrated in U.S. Published Patent Application No. 2016/0222174.

The recombinant block copolymer polypeptides based on spider silk sequences produced by gene expression in a recombinant prokaryotic or eukaryotic system can be purified according to methods known in the art. In a preferred embodiment, a commercially available expression/secretion system can be used, whereby the recombinant polypeptide is expressed and thereafter secreted from the host cell, to be easily purified from the surrounding medium. If expression/secretion vectors are not used, an alternative approach involves purifying the recombinant block copolymer polypeptide from cell lysates (remains of cells following disruption of cellular integrity) derived from prokaryotic or eukaryotic cells in which a polypeptide was expressed. Methods for generation of such cell lysates are known to those of skill in the art. In some embodiments, recombinant block copolymer polypeptides are isolated from cell culture supernatant.

Recombinant block copolymer polypeptide may be purified by affinity separation, such as by immunological interaction with antibodies that bind specifically to the recombinant polypeptide or nickel columns for isolation of recombinant polypeptides tagged with 6-8 histidine residues at their N-terminus or C-terminus. Alternative tags may comprise the FLAG epitope or the hemagglutinin epitope. Such methods are commonly used by skilled practitioners.

A solution of such polypeptides (i.e., recombinant silk protein) may then be prepared and used as described herein.

In another embodiment, recombinant silk protein may be prepared according to the methods described in U.S. Patent No. 8,642,734, the entirety of which is incorporated herein, and used as described herein.

In an embodiment, a recombinant spider silk protein is provided. The spider silk protein typically consists of from 170 to 760 amino acid residues, such as from 170 to

600 amino acid residues, preferably from 280 to 600 amino acid residues, such as from 300 to 400 amino acid residues, more preferably from 340 to 380 amino acid residues. The small size is advantageous because longer spider silk proteins tend to form amorphous aggregates, which require use of harsh solvents for solubilization and polymerization. The recombinant spider silk protein may contain more than 760 residues, in particular in cases where the spider silk protein contains more than two fragments derived from the N-terminal part of a spider silk protein. The spider silk protein comprises an N-terminal fragment consisting of at least one fragment (NT) derived from the corresponding part of a spider silk protein, and a repetitive fragment (REP) derived from the corresponding internal fragment of a spider silk protein. Optionally, the spider silk protein comprises a C-terminal fragment (CT) derived from the corresponding fragment of a spider silk protein. The spider silk protein comprises typically a single fragment (NT) derived from the N-terminal part of a spider silk protein, but in preferred embodiments, the N-terminal fragment include at least two, such as two fragments (NT) derived from the N-terminal part of a spider silk protein. Thus, the spidroin can schematically be represented by the formula $NT_m\text{-REP}$, and alternatively $NT_m\text{-REP-CT}$, where m is an integer that is 1 or higher, such as 2 or higher, preferably in the ranges of 1-2, 1-4, 1-6, 2-4 or 2-6. Preferred spidroins can schematically be represented by the formulas $NT_2\text{-REP}$ or $NT\text{-REP}$, and alternatively $NT_2\text{-REP-CT}$ or $NT\text{-REP-CT}$. The protein fragments are covalently coupled, typically via a peptide bond. In one embodiment, the spider silk protein consists of the NT fragment(s) coupled to the REP fragment, which REP fragment is optionally coupled to the CT fragment.

In one embodiment, the first step of the method of producing polymers of an isolated spider silk protein involves expression of a polynucleic acid molecule which encodes the spider silk protein in a suitable host, such as *Escherichia coli*. The thus obtained protein is isolated using standard procedures. Optionally, lipopolysaccharides and other pyrogens are actively removed at this stage.

In the second step of the method of producing polymers of an isolated spider silk protein, a solution of the spider silk protein in a liquid medium is provided. By the terms “soluble” and “in solution” is meant that the protein is not visibly aggregated and does not precipitate from the solvent at 60,000×g. The liquid medium can be any suitable

medium, such as an aqueous medium, preferably a physiological medium, typically a buffered aqueous medium, such as a 10-50 mM Tris-HCl buffer or phosphate buffer. The liquid medium has a pH of 6.4 or higher and/or an ion composition that prevents polymerization of the spider silk protein. That is, the liquid medium has either a pH of 6.4 or higher or an ion composition that prevents polymerization of the spider silk protein, or both.

Ion compositions that prevent polymerization of the spider silk protein can readily be prepared by the skilled person utilizing the methods disclosed herein. A preferred ion composition that prevents polymerization of the spider silk protein has an ionic strength of more than 300 mM. Specific examples of ion compositions that prevent polymerization of the spider silk protein include above 300 mM NaCl, 100 mM phosphate and combinations of these ions having desired preventive effect on the polymerization of the spider silk protein, e.g. a combination of 10 mM phosphate and 300 mM NaCl.

The presence of an NT fragment improves the stability of the solution and prevents polymer formation under these conditions. This can be advantageous when immediate polymerization may be undesirable, e.g. during protein purification, in preparation of large batches, or when other conditions need to be optimized. It is preferred that the pH of the liquid medium is adjusted to 6.7 or higher, such as 7.0 or higher, or even 8.0 or higher, such as up to 10.5, to achieve high solubility of the spider silk protein. It can also be advantageous that the pH of the liquid medium is adjusted to the range of 6.4-6.8, which provides sufficient solubility of the spider silk protein but facilitates subsequent pH adjustment to 6.3 or lower.

In the third step, the properties of the liquid medium are adjusted to a pH of 6.3 or lower and ion composition that allows polymerization. That is, if the liquid medium wherein the spider silk protein is dissolved has a pH of 6.4 or higher, the pH is decreased to 6.3 or lower. The skilled person is well aware of various ways of achieving this, typically involving addition of a strong or weak acid. If the liquid medium wherein the spider silk protein is dissolved has an ion composition that prevents polymerization, the ion composition is changed so as to allow polymerization. The skilled person is well aware of various ways of achieving this, e.g. dilution, dialysis or gel filtration. If

required, this step involves both decreasing the pH of the liquid medium to 6.3 or lower and changing the ion composition so as to allow polymerization. It is preferred that the pH of the liquid medium is adjusted to 6.2 or lower, such as 6.0 or lower. In particular, it may be advantageous from a practical point of view to limit the pH drop from 6.4 or 6.4-6.8 in the preceding step to 6.3 or 6.0-6.3, e.g. 6.2 in this step. In a preferred embodiment, the pH of the liquid medium of this step is 3 or higher, such as 4.2 or higher. The resulting pH range, e.g. 4.2-6.3 promotes rapid polymerization,

In the fourth step, the spider silk protein is allowed to polymerize in the liquid medium having pH of 6.3 or lower and an ion composition that allows polymerization of the spider silk protein. Although the presence of the NT fragment improves solubility of the spider silk protein at a pH of 6.4 or higher and/or an ion composition that prevents polymerization of the spider silk protein, it accelerates polymer formation at a pH of 6.3 or lower when the ion composition allows polymerization of the spider silk protein. The resulting polymers are preferably solid and macroscopic, and they are formed in the liquid medium having a pH of 6.3 or lower and an ion composition that allows polymerization of the spider silk protein. In a preferred embodiment, the pH of the liquid medium of this step is 3 or higher, such as 4.2 or higher. The resulting pH range, e.g. 4.2-6.3 promotes rapid polymerization, Resulting polymer may be provided at the molecular weights described herein and prepared as a solution form that may be used as necessary for article coatings.

Ion compositions that allow polymerization of the spider silk protein can readily be prepared by the skilled person utilizing the methods disclosed herein. A preferred ion composition that allows polymerization of the spider silk protein has an ionic strength of less than 300 mM. Specific examples of ion compositions that allow polymerization of the spider silk protein include 150 mM NaCl, 10 mM phosphate, 20 mM phosphate and combinations of these ions lacking preventive effect on the polymerization of the spider silk protein, e.g. a combination of 10 mM phosphate or 20 mM phosphate and 150 mM NaCl. It is preferred that the ionic strength of this liquid medium is adjusted to the range of 1-250 mM.

Without desiring to be limited to any specific theory, it is envisaged that the NT fragments have oppositely charged poles, and that environmental changes in pH affects

the charge balance on the surface of the protein followed by polymerization, whereas salt inhibits the same event.

At neutral pH, the energetic cost of burying the excess negative charge of the acidic pole may be expected to prevent polymerization. However, as the dimer approaches its isoelectric point at lower pH, attractive electrostatic forces will eventually become dominant, explaining the observed salt and pH-dependent polymerization behavior of NT and NT-containing minispidroins. It is proposed that, in some embodiments, pH-induced NT polymerization, and increased efficiency of fiber assembly of NT-minispidroins, are due to surface electrostatic potential changes, and that clustering of acidic residues at one pole of NT shifts its charge balance such that the polymerization transition occurs at pH values of 6.3 or lower.

In a fifth step, the resulting, preferably solid spider silk protein polymers are isolated from said liquid medium. Optionally, this step involves actively removing lipopolysaccharides and other pyrogens from the spidroin polymers.

Without desiring to be limited to any specific theory, it has been observed that formation of spidroin polymers progresses via formation of water-soluble spidroin dimers. The present disclosure thus also provides a method of producing dimers of an isolated spider silk protein, wherein the first two method steps are as described above. The spider silk proteins are present as dimers in a liquid medium at a pH of 6.4 or higher and/or an ion composition that prevents polymerization of said spider silk protein. The third step involves isolating the dimers obtained in the second step, and optionally removal of lipopolysaccharides and other pyrogens. In a preferred embodiment, the spider silk protein polymer of the disclosure consists of polymerized protein dimers. The present disclosure thus provides a novel use of a spider silk protein, preferably those disclosed herein, for producing dimers of the spider silk protein.

According to another aspect, the disclosure provides a polymer of a spider silk protein as disclosed herein. In an embodiment, the polymer of this protein is obtainable by any one of the methods therefor according to the disclosure. Thus, the disclosure provides various uses of recombinant spider silk protein, preferably those disclosed herein, for producing polymers of the spider silk protein as recombinant silk based coatings. According to one embodiment, the present disclosure provides a novel use of a

dimer of a spider silk protein, preferably those disclosed herein, for producing polymers of the isolated spider silk protein as recombinant silk based coatings. In these uses, it is preferred that the polymers are produced in a liquid medium having a pH of 6.3 or lower and an ion composition that allows polymerization of said spider silk protein. In an embodiment, the pH of the liquid medium is 3 or higher, such as 4.2 or higher. The resulting pH range, e.g. 4.2-6.3 promotes rapid polymerization,

Using the method(s) of the present disclosure, it is possible to control the polymerization process, and this allows for optimization of parameters for obtaining silk polymers with desirable properties and shapes.

In an embodiment, the recombinant silk proteins described herein, include those described in U.S. patent No. 8,642,734, the entirety of which is incorporated by reference.

In another embodiment, the recombinant silk proteins described herein may be prepared according to the methods described in U.S. Patent No. 9,051,453, the entirety of which is incorporated herein by reference.

An amino acid sequence represented by SEQ ID NO: 1 of U.S. Patent No. 9,051,453 is identical to an amino acid sequence that is composed of 50 amino acid residues of an amino acid sequence of ADF3 at the C-terminal (NCBI Accession No.: AAC47010, GI: 1263287). An amino acid sequence represented by SEQ ID NO: 2 of U.S. Patent No. 9,051,453 is identical to an amino acid sequence represented by SEQ ID NO: 1 of U.S. Patent No. 9,051,453 from which 20 residues have been removed from the C-terminal. An amino acid sequence represented by SEQ ID NO: 3 of U.S. Patent No. 9,051,453 is identical to an amino acid sequence represented by SEQ ID NO: 1 from which 29 residues have been removed from the C-terminal.

An example of the polypeptide that contains units of the amino acid sequence represented by the formula 1: REP1-REP2 (1) and that has, at a C-terminal, an amino acid sequence represented by any of SEQ ID NOS: 1 to 3 or an amino acid sequence having a homology of 90% or more with the amino acid sequence represented by any of SEQ ID NOS: 1 to 3 of U.S. Patent No. 9,051,453 is a polypeptide having an amino acid sequence represented by SEQ ID NO: 8 of U.S. Patent No. 9,051,453. The polypeptide having the amino acid sequence represented by SEQ ID NO: 8 of U.S. Patent No.

9,051,453 is obtained by the following mutation: in an amino acid sequence of ADF3 (NCBI Accession No.: AAC47010, GI: 1263287) to the N-terminal of which has been added an amino acid sequence (SEQ ID NO: 5 of U.S. Patent No. 9,051,453) composed of a start codon, His 10 tags and an HRV3C Protease (Human rhinovirus 3C Protease) recognition site, 1st to 13th repetitive regions are about doubled and the translation ends at the 1154th amino acid residue. In the polypeptide having the amino acid sequence represented by SEQ ID NO: 8 of U.S. Patent No. 9,051,453, the C-terminal sequence is identical to the amino acid sequence represented by SEQ ID NO: 3.

Further, the polypeptide that contains units of the amino acid sequence represented by the formula 1: REP1-REP2 (1) and that has, at a C-terminal, an amino acid sequence represented by any of SEQ ID NOS: 1 to 3 of U.S. Patent No. 9,051,453 or an amino acid sequence having a homology of 90% or more with the amino acid sequence represented by any of SEQ ID NOS: 1 to 3 of U.S. Patent No. 9,051,453 may be a protein that has an amino acid sequence represented by SEQ ID NO: 8 of U.S. Patent No. 9,051,453 in which one or a plurality of amino acids have been substituted, deleted, inserted and/or added and that has a repetitious region composed of a crystal region and an amorphous region.

Further, an example of the polypeptide containing two or more units of the amino acid sequence represented by the formula 1: REP1-REP2 (1) is a recombinant protein derived from ADF4 having an amino acid sequence represented by SEQ ID NO: 15 of U.S. Patent No. 9,051,453. The amino acid sequence represented by SEQ ID NO: 15 of U.S. Patent No. 9,051,453 is an amino acid sequence obtained by adding the amino acid sequence (SEQ ID NO: 5 of U.S. Patent No. 9,051,453) composed of a start codon, His 10 tags and an HRV3C Protease (Human rhinovirus 3C Protease) recognition site, to the N-terminal of a partial amino acid sequence of ADF4 obtained from the NCBI database (NCBI Accession No.: AAC47011, GI: 1263289). Further, the polypeptide containing two or more units of the amino acid sequence represented by the formula 1: REP1-REP2 (1) may be a polypeptide that has an amino acid sequence represented by SEQ ID NO: 15 of U.S. Patent No. 9,051,453 in which one or a plurality of amino acids have been substituted, deleted, inserted and/or added and that has a repetitious region composed of a crystal region and an amorphous region. Further, an example of the polypeptide

containing two or more units of the amino acid sequence represented by the formula 1: REP1-REP2 (1) is a recombinant protein derived from MaSp2 that has an amino acid sequence represented by SEQ ID NO: 17 of U.S. Patent No. 9,051,453. The amino acid sequence represented by SEQ ID NO: 17 of U.S. Patent No. 9,051,453 is an amino acid sequence obtained by adding the amino acid sequence (SEQ ID NO: 5 of U.S. Patent No. 9,051,453) composed of a start codon, His 10 tags and an HRV3C Protease (Human rhinovirus 3C Protease) recognition site, to the N-terminal of a partial sequence of MaSp2 obtained from the NCBI web database (NCBI Accession No.: AAT75313, GI: 50363147). Furthermore, the polypeptide containing two or more units of the amino acid sequence represented by the formula 1: REP1-REP2 (1) may be a polypeptide that has an amino acid sequence represented by SEQ ID NO: 17 of U.S. Patent No. 9,051,453 in which one or a plurality of amino acids have been substituted, deleted, inserted and/or added and that has a repetitious region composed of a crystal region and an amorphous region.

Examples of the polypeptide derived from flagelliform silk proteins include a polypeptide containing 10 or more units of an amino acid sequence represented by the formula 2: REP3 (2), preferably a polypeptide containing 20 or more units thereof, and more preferably a polypeptide containing 30 or more units thereof. In the case of producing a recombinant protein using a microbe such as *Escherichia coli* as a host, the molecular weight of the polypeptide derived from flagelliform silk proteins is preferably 500 kDa or less, more preferably 300 kDa or less, and further preferably 200 kDa or less, in terms of productivity.

In the formula (2), the REP 3 indicates an amino acid sequence composed of Gly-Pro-Gly-Gly-X, where X indicates an amino acid selected from the group consisting of Ala, Ser, Tyr and Val.

A major characteristic of the spider silk is that the flagelliform silk does not have a crystal region, but has a repetitious region composed of an amorphous region. Since the major dragline silk and the like have a repetitious region composed of a crystal region and an amorphous region, they are expected to have both high stress and stretchability. Meanwhile, as to the flagelliform silk, although the stress is inferior to that of the major

dragline silk, the stretchability is high. The reason for this is considered to be that most of the flagelliform silk is composed of amorphous regions.

An example of the polypeptide containing 10 or more units of the amino acid sequence represented by the formula 2: REP3 (2) is a recombinant protein derived from flagelliform silk proteins having an amino acid sequence represented by SEQ ID NO: 19 of U.S. Patent No. 9,051,453. The amino acid sequence represented by SEQ ID NO: 19 of U.S. Patent No. 9,051,453 is an amino acid sequence obtained by combining a partial sequence of flagelliform silk protein of *Nephila clavipes* obtained from the NCBI database (NCBI Accession No.: AAF36090, GI: 7106224), specifically, an amino acid sequence thereof from the 1220th residue to the 1659th residue from the N-terminal that corresponds to repetitive sections and motifs (referred to as a PR1 sequence), with a partial sequence of flagelliform silk protein of *Nephila clavipes* obtained from the NCBI database (NCBI Accession No.: AAC38847, GI: 2833649), specifically, a C-terminal amino acid sequence thereof from the 816th residue to the 907th residue from the C-terminal, and thereafter adding the amino acid sequence (SEQ ID NO: 5 of U.S. Patent No. 9,051,453) composed of a start codon, His 10 tags and an HRV3C Protease recognition site, to the N-terminal of the combined sequence. Further, the polypeptide containing 10 or more units of the amino acid sequence represented by the formula 2: REP3 (2) may be a polypeptide that has an amino acid sequence represented by SEQ ID NO: 19 of U.S. Patent No. 9,051,453 in which one or a plurality of amino acids have been substituted, deleted, inserted and/or added and that has a repetitious region composed of an amorphous region.

The polypeptide can be produced using a host that has been transformed by an expression vector containing a gene encoding a polypeptide. A method for producing a gene is not limited particularly, and it may be produced by amplifying a gene encoding a natural spider silk protein from a cell derived from spiders by a polymerase chain reaction (PCR), etc., and cloning it, or may be synthesized chemically. Also, a method for chemically synthesizing a gene is not limited particularly, and it can be synthesized as follows, for example: based on information of amino acid sequences of natural spider silk proteins obtained from the NCBI web database, etc., oligonucleotides that have been synthesized automatically with AKTA oligopilot plus 10/100 (GE Healthcare Japan

Corporation) are linked by PCR, etc. At this time, in order to facilitate the purification and observation of protein, it is possible to synthesize a gene that encodes a protein having an amino acid sequence of the above-described amino acid sequence to the N-terminal of which has been added an amino acid sequence composed of a start codon and His 10 tags.

Examples of the expression vector include a plasmid, a phage, a virus, and the like that can express protein based on a DNA sequence. The plasmid-type expression vector is not limited particularly as long as it allows a target gene to be expressed in a host cell and it can amplify itself. For example, in the case of using *Escherichia coli* Rosetta (DE3) as a host, a pET22b(+) plasmid vector, a pCold plasmid vector, and the like can be used. Among these, in terms of productivity of protein, it is preferable to use the pET22b(+) plasmid vector. Examples of the host include animal cells, plant cells, microbes, etc.

The polypeptide used in the present disclosure is preferably a polypeptide derived from ADF3, which is one of two principal dragline silk proteins of *Araneus diadematus*. This polypeptide has advantages of basically having high strength-elongation and toughness and of being synthesized easily.

Accordingly, the recombinant silk protein (e.g., the recombinant spider silk-based protein) used in accordance with the embodiments, articles, and/or methods described herein, may include one or more recombinant silk proteins described above or recited in U.S. Patent Nos. 8,173,772, 8,278,416, 8,618,255, 8,642,734, 8,691,581, 8,729,235, 9,115,204, 9,157,070, 9,309,299, 9,644,012, 9,708,376, 9,051,453, 9,617,315, 9,968,682, 9,689,089, 9,732,125, 9,856,308, 9,926,348, 10,065,997, 10,316,069, and 10,329,332; and U.S. Patent Publication Nos. 2009/0226969, 2011/0281273, 2012/0041177, 2013/0065278, 2013/0115698, 2013/0316376, 2014/0058066, 2014/0079674, 2014/0245923, 2015/0087046, 2015/0119554, 2015/0141618, 2015/0291673, 2015/0291674, 2015/0239587, 2015/0344542, 2015/0361144, 2015/0374833, 2015/0376247, 2016/0024464, 2017/0066804, 2017/0066805, 2015/0293076, 2016/0222174, 2017/0283474, 2017/0088675, 2019/0135880, 2015/0329587, 2019/0040109, 2019/0135881, 2019/0177363, 2019/0225646, 2019/0233481, 2019/0031842, 2018/0355120, 2019/0186050, 2019/0002644, 2020/0031887,

2018/0273590, 20191/094403, 2019/0031843, 2018/0251501, 2017/0066805, 2018/0127553, 2019/0329526, 2020/0031886, 2018/0080147, 2019/0352349, 2020/0043085, 2019/0144819, 2019/0228449, 2019/0340666, 2020/0000091, 2019/0194710, 2019/0151505, 2018/0265555, 2019/0352330, 2019/0248847, and 2019/0378191, the entirety of which are incorporated herein by reference.

Silk Fibroin-like Protein Fragments

The recombinant silk protein in this disclosure comprises synthetic proteins which are based on repeat units of natural silk proteins. Besides the synthetic repetitive silk protein sequences, these can additionally comprise one or more natural nonrepetitive silk protein sequences. As used herein, “silk fibroin-like protein fragments” refer to protein fragments having a molecular weight and polydispersity as defined herein, and a certain degree of homology to a protein selected from native silk protein, fibroin heavy chain, fibroin light chain, or any protein comprising one or more GAGAGS hexa amino acid repeating units. In some embodiments, a degree of homology is selected from about 99%, about 98%, about 97%, about 96%, about 95%, about 94%, about 93%, about 92%, about 91%, about 90%, about 89%, about 88%, about 87%, about 86%, about 85%, about 84%, about 83%, about 82%, about 81%, about 80%, about 79%, about 78%, about 77%, about 76%, about 75%, or less than 75%.

As described herein, a protein such as native silk protein, fibroin heavy chain, fibroin light chain, or any protein comprising one or more GAGAGS hexa amino acid repeating units includes between about 9% and about 45% glycine, or about 9% glycine, or about 10% glycine, about 43% glycine, about 44% glycine, about 45% glycine, or about 46% glycine. As described herein, a protein such as native silk protein, fibroin heavy chain, fibroin light chain, or any protein comprising one or more GAGAGS hexa amino acid repeating units includes between about 13% and about 30% alanine, or about 13% alanine, or about 28% alanine, or about 29% alanine, or about 30% alanine, or about 31% alanine. As described herein, a protein such as native silk protein, fibroin heavy chain, fibroin light chain, or any protein comprising one or more GAGAGS hexa amino acid repeating units includes between 9% and about 12% serine, or about 9% serine, or about 10% serine, or about 11% serine, or about 12% serine.

In some embodiments, a silk fibroin-like protein described herein includes about 5%, about 6%, about 7%, about 8%, about 9%, about 10%, about 11%, about 12%, about 13%, about 14%, about 15%, about 16%, about 17%, about 18%, about 19%, about 20%, about 21%, about 22%, about 23 %, about 24%, about 25%, about 26%, about 27%, about 28%, about 29%, about 30%, about 31%, about 32%, about 33%, about 34%, about 35%, about 36%, about 37%, about 38%, about 39%, about 40%, about 41%, about 42%, about 43%, about 44%, about 45%, about 46%, about 47%, about 48%, about 49%, about 50%, about 51%, about 52%, about 53%, about 54%, or about 55% glycine. In some embodiments, a silk fibroin-like protein described herein includes about 13%, about 14%, about 15%, about 16%, about 17%, about 18%, about 19%, about 20%, about 21%, about 22%, about 23%, about 24%, about 25%, about 26%, about 27%, about 28%, about 29%, about 30%, about 31%, about 32%, about 33%, about 34%, about 35%, about 36%, about 37%, about 38%, or about 39% alanine. In some embodiments, a silk fibroin-like protein described herein includes about 2%, about 3%, about 4%, about 5%, about 6%, about 7%, about 8%, about 9%, about 10%, about 11%, about 12%, about 13%, about 14%, about 15%, about 16%, about 17%, about 18%, about 19%, about 20%, about 21%, or about 22% serine. In some embodiments, a silk fibroin-like protein described herein may include independently any amino acid known to be included in natural fibroin. In some embodiments, a silk fibroin-like protein described herein may exclude independently any amino acid known to be included in natural fibroin. In some embodiments, on average 2 out of 6 amino acids, 3 out of 6 amino acids, or 4 out of 6 amino acids in a silk fibroin-like protein described herein is glycine. In some embodiments, on average 1 out of 6 amino acids, 2 out of 6 amino acids, or 3 out of 6 amino acids in a silk fibroin-like protein described herein is alanine. In some embodiments, on average none out of 6 amino acids, 1 out of 6 amino acids, or 2 out of 6 amino acids in a silk fibroin-like protein described herein is serine.

Other Properties of SPF

Compositions of the present disclosure are “biocompatible” or otherwise exhibit “biocompatibility” meaning that the compositions are compatible with living tissue or a living system by not being toxic, injurious, or physiologically reactive and not causing immunological rejection or an inflammatory response. Such biocompatibility can be

evidenced by participants topically applying compositions of the present disclosure on their skin for an extended period of time. In an embodiment, the extended period of time is about 3 days. In an embodiment, the extended period of time is about 7 days. In an embodiment, the extended period of time is about 14 days. In an embodiment, the extended period of time is about 21 days. In an embodiment, the extended period of time is about 30 days. In an embodiment, the extended period of time is selected from the group consisting of about 1 month, about 2 months, about 3 months, about 4 months, about 5 months, about 6 months, about 7 months, about 8 months, about 9 months, about 10 months, about 11 months, about 12 months, and indefinitely. For example, in some embodiments, the coatings described herein are biocompatible coatings.

In some embodiments, compositions described herein, which may be biocompatible compositions (e.g., biocompatible coatings that include silk), may be evaluated and comply with International Standard ISO 10993-1, titled the “Biological evaluation of medical devices – Part 1: Evaluation and testing within a risk management process.” In some embodiments, compositions described herein, which may be biocompatible compositions, may be evaluated under ISO 10693-1 for one or more of cytotoxicity, sensitization, hemocompatibility, pyrogenicity, implantation, genotoxicity, carcinogenicity, reproductive and developmental toxicity, and degradation.

Compositions of the present disclosure are “hypoallergenic” meaning that they are relatively unlikely to cause an allergic reaction. Such hypoallergenicity can be evidenced by participants topically applying compositions of the present disclosure on their skin for an extended period of time. In an embodiment, the extended period of time is about 3 days. In an embodiment, the extended period of time is about 7 days. In an embodiment, the extended period of time is about 14 days. In an embodiment, the extended period of time is about 21 days. In an embodiment, the extended period of time is about 30 days. In an embodiment, the extended period of time is selected from the group consisting of about 1 month, about 2 months, about 3 months, about 4 months, about 5 months, about 6 months, about 7 months, about 8 months, about 9 months, about 10 months, about 11 months, about 12 months, and indefinitely.

In an embodiment, the stability of a composition of the present disclosure is about 1 day. In an embodiment, the stability of a composition of the present disclosure is about

2 days. In an embodiment, the stability of a composition of the present disclosure is about 3 days. In an embodiment, the stability of a composition of the present disclosure is about 4 days. In an embodiment, the stability of a composition of the present disclosure is about 5 days. In an embodiment, the stability of a composition of the present disclosure is about 6 days. In an embodiment, the stability of a composition of the present disclosure is about 7 days. In an embodiment, the stability of a composition of the present disclosure is about 8 days. In an embodiment, the stability of a composition of the present disclosure is about 9 days. In an embodiment, the stability of a composition of the present disclosure is about 10 days.

In an embodiment, the stability of a composition of the present disclosure is about 11 days, about 12 days, about 13 days, about 14 days, about 15 days, about 16 days, about 17 days, about 18 days, about 19 days, about 20 days, about 21 days, about 22 days, about 23 days, about 24 days, about 25 days, about 26 days, about 27 days, about 28 days, about 29 days, or about 30 days.

In an embodiment, the stability of a composition of the present disclosure is 10 days to 6 months. In an embodiment, the stability of a composition of the present disclosure is 6 months to 12 months. In an embodiment, the stability of a composition of the present disclosure is 12 months to 18 months. In an embodiment, the stability of a composition of the present disclosure is 18 months to 24 months. In an embodiment, the stability of a composition of the present disclosure is 24 months to 30 months. In an embodiment, the stability of a composition of the present disclosure is 30 months to 36 months. In an embodiment, the stability of a composition of the present disclosure is 36 months to 48 months. In an embodiment, the stability of a composition of the present disclosure is 48 months to 60 months.

In an embodiment, a SPF composition of the present disclosure is not soluble in an aqueous solution due to the crystallinity of the protein. In an embodiment, a SPF composition of the present disclosure is soluble in an aqueous solution. In an embodiment, the SPF of a composition of the present disclosure include a crystalline portion of about two-thirds and an amorphous region of about one-third. In an embodiment, the SPF of a composition of the present disclosure include a crystalline portion of about one-half and an amorphous region of about one-half. In an embodiment,

the SPF of a composition of the present disclosure include a 99% crystalline portion and a 1% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 95% crystalline portion and a 5% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 90% crystalline portion and a 10% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 85% crystalline portion and a 15% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 80% crystalline portion and a 20% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 75% crystalline portion and a 25% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 70% crystalline portion and a 30% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 65% crystalline portion and a 35% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 60% crystalline portion and a 40% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 50% crystalline portion and a 50% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 40% crystalline portion and a 60% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 35% crystalline portion and a 65% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 30% crystalline portion and a 70% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 25% crystalline portion and a 75% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 20% crystalline portion and a 80% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 15% crystalline portion and a 85% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 10% crystalline portion and a 90% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 5% crystalline portion and a 95% amorphous region. In an embodiment, the SPF of a composition of the present disclosure include a 1% crystalline portion and a 99% amorphous region.

As used herein, the term “substantially free of inorganic residuals” means that the composition exhibits residuals of 0.1 % (w/w) or less. In an embodiment, substantially

free of inorganic residuals refers to a composition that exhibits residuals of 0.05% (w/w) or less. In an embodiment, substantially free of inorganic residuals refers to a composition that exhibits residuals of 0.01 % (w/w) or less. In an embodiment, the amount of inorganic residuals is between 0 ppm (“non-detectable” or “ND”) and 1000 ppm. In an embodiment, the amount of inorganic residuals is ND to about 500 ppm. In an embodiment, the amount of inorganic residuals is ND to about 400 ppm. In an embodiment, the amount of inorganic residuals is ND to about 300 ppm. In an embodiment, the amount of inorganic residuals is ND to about 200 ppm. In an embodiment, the amount of inorganic residuals is ND to about 100 ppm. In an embodiment, the amount of inorganic residuals is between 10 ppm and 1000 ppm.

As used herein, the term “substantially free of organic residuals” means that the composition exhibits residuals of 0.1 % (w/w) or less, in an embodiment, substantially free of organic residuals refers to a composition that exhibits residuals of 0.05% (w/w) or less. In an embodiment, substantially free of organic residuals refers to a composition that exhibits residuals of 0.01% (w/w) or less. In an embodiment, the amount of organic residuals is between 0 ppm (“non-detectable” or “ND”) and 1000 ppm. In an embodiment, the amount of organic residuals is ND to about 500 ppm. In an embodiment, the amount of organic residuals is ND to about 400 ppm. In an embodiment, the amount of organic residuals is ND to about 300 ppm. In an embodiment, the amount of organic residuals is ND to about 200 ppm. In an embodiment, the amount of organic residuals is ND to about 100 ppm. In an embodiment, the amount of organic residuals is between 10 ppm and 1000 ppm.

Compositions of the present disclosure exhibit “biocompatibility” meaning that the compositions are compatible with living tissue or a living system by not being toxic, injurious, or physiologically reactive and not causing immunological rejection. Such biocompatibility can be evidenced by participants topically applying compositions of the present disclosure on their skin for an extended period of time. In an embodiment, the extended period of time is about 3 days. In an embodiment, the extended period of time is about 7 days, in an embodiment, the extended period of time is about 14 days, in an embodiment, the extended period of time is about 21 days. In an embodiment, the extended period of time is about 30 days. In an embodiment, the extended period of time

is selected from the group consisting of about 1 month, about 2 months, about 3 months, about 4 months, about 5 months, about 6 months, about 7 months, about 8 months, about 9 months, about 10 months, about 11 months, about 12 months, and indefinitely.

Compositions of the present disclosure are “hypoallergenic” meaning that they are relatively unlikely to cause an allergic reaction. Such hypoallergenicity can be evidenced by participants topically applying compositions of the present disclosure on their skin for an extended period of time. In an embodiment, the extended period of time is about 3 days. In an embodiment, the extended period of time is about 7 days. In an embodiment, the extended period of time is about 14 days. In an embodiment, the extended period of time is about 21 days. In an embodiment, the extended period of time is about 30 days. In an embodiment, the extended period of time is selected from the group consisting of about 1 month, about 2 months, about 3 months, about 4 months, about 5 months, about 6 months, about 7 months, about 8 months, about 9 months, about 10 months, about 11 months, about 12 months, and indefinitely.

Following are non-limiting examples of suitable ranges for various parameters in and for preparation of the silk solutions of the present disclosure. The silk solutions of the present disclosure may include one or more, but not necessarily all, of these parameters and may be prepared using various combinations of ranges of such parameters.

In an embodiment, the percent SPF in the solution is less than 30.0 wt. %. In an embodiment, the percent SPF in the solution is less than 25.0 wt. %. In an embodiment, the percent SPF in the solution is less than 20.0 wt. %. In an embodiment, the percent SPF in the solution is less than 19.0 wt. %. In an embodiment, the percent SPF in the solution is less than 18.0 wt. %. In an embodiment, the percent SPF in the solution is less than 17.0 wt. %. In an embodiment, the percent SPF in the solution is less than 16.0 wt. %. In an embodiment, the percent SPF in the solution is less than 15.0 wt. %. In an embodiment, the percent SPF in the solution is less than 14.0 wt. %. In an embodiment, the percent SPF in the solution is less than 13.0 wt. %. In an embodiment, the percent SPF in the solution is less than 12.0 wt. %. In an embodiment, the percent SPF in the solution is less than 11.0 wt. %. In an embodiment, the percent SPF in the solution is less than 10.0 wt. %. In an embodiment, the percent SPF in the solution is less than 9.0 wt. %. In an embodiment, the percent SPF in the solution is less than 8.0 wt. %. In an

SPF in the solution is greater than 11.0 wt. %. In an embodiment, the percent SPF in the solution is greater than 12.0 wt. %. In an embodiment, the percent SPF in the solution is greater than 13.0 wt. %. In an embodiment, the percent SPF in the solution is greater than 14.0 wt. %. In an embodiment, the percent SPF in the solution is greater than 15.0 wt. %. In an embodiment, the percent SPF in the solution is greater than 16.0 wt. %. In an embodiment, the percent SPF in the solution is greater than 17.0 wt. %. In an embodiment, the percent SPF in the solution is greater than 18.0 wt. %. In an embodiment, the percent SPF in the solution is greater than 19.0 wt. %. In an embodiment, the percent SPF in the solution is greater than 20.0 wt. %. In an embodiment, the percent SPF in the solution is greater than 25.0 wt. %.

In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 30.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 25.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 20.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 15.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 10.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 9.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 8.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 7.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 6.5 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 6.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 5.5 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 5.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 4.5 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 4.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 3.5 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 3.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 2.5 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 2.0 wt. %. In an embodiment, the percent SPF in

the solution ranges from about 0.1 wt. % to about 2.4 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.5 wt. % to about 5.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.5 wt. % to about 4.5 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.5 wt. % to about 4.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.5 wt. % to about 3.5 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.5 wt. % to about 3.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.5 wt. % to about 2.5 wt. %. In an embodiment, the percent SPF in the solution ranges from about 1.0 wt. % to about 4.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 1.0 wt. % to about 3.5 wt. %. In an embodiment, the percent SPF in the solution ranges from about 1.0 wt. % to about 3.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 1.0 wt. % to about 2.5 wt. %. In an embodiment, the percent SPF in the solution ranges from about 1.0 wt. % to about 2.4 wt. %. In an embodiment, the percent SPF in the solution ranges from about 1.0 wt. % to about 2.0 wt. %.

In an embodiment, the percent SPF in the solution ranges from about 20.0 wt. % to about 30.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 10.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 1.0 wt. % to about 10.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 2 wt. % to about 10.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 0.1 wt. % to about 6.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 6.0 wt. % to about 10.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 6.0 wt. % to about 8.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 6.0 wt. % to about 9.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 10.0 wt. % to about 20.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 11.0 wt. % to about 19.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 12.0 wt. % to about 18.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 13.0 wt. % to about 17.0 wt. %. In an embodiment, the percent SPF in the solution ranges from about 14.0 wt. % to about 16.0 wt. %. In an embodiment, the percent SPF in the solution is about 1.0 wt. %. In an

embodiment, the percent SPF in the solution is about 1.5 wt. %. In an embodiment, the percent SPF in the solution is about 2.0 wt.%. In an embodiment, the percent SPF in the solution is about 2.4 wt. %. In an embodiment, the percent SPF in the solution is 3.0 wt. %. In an embodiment, the percent SPF in the solution is 3.5 wt. %. In an embodiment, the percent SPF in the solution is about 4.0 wt. %. In an embodiment, the percent SPF in the solution is about 4.5 wt. %. In an embodiment, the percent SPF in the solution is about 5.0 wt. %. In an embodiment, the percent SPF in the solution is about 5.5 wt. %. In an embodiment the percent SPF in the solution is about 6.0 wt. %. In an embodiment, the percent SPF in the solution is about 6.5 wt. %. In an embodiment, the percent SPF in the solution is about 7.0 wt. %. In an embodiment, the percent SPF in the solution is about 7.5 wt. %. In an embodiment, the percent SPF in the solution is about 8.0 wt. %. In an embodiment, the percent SPF in the solution is about 8.5 wt. %. In an embodiment, the percent SPF in the solution is about 9.0 wt. %. In an embodiment, the percent SPF in the solution is about 9.5 wt. %. In an embodiment, the percent SPF in the solution is about 10.0 wt. %.

In an embodiment, the percent sericin in the solution is non-detectable to 25.0 wt. %. In an embodiment, the percent sericin in the solution is non-detectable to 5.0 wt. %. In an embodiment, the percent sericin in the solution is 1.0 wt. %. In an embodiment, the percent sericin in the solution is 2.0 wt. %. In an embodiment, the percent sericin in the solution is 3.0 wt. %. In an embodiment, the percent sericin in the solution is 4.0 wt. %. In an embodiment, the percent sericin in the solution is 5.0 wt. %. In an embodiment, the percent sericin in the solution is 10.0 wt. %. In an embodiment, the percent sericin in the solution is 25.0 wt. %.

In some embodiments, the silk fibroin protein fragments of the present disclosure are shelf stable (they will not slowly or spontaneously gel when stored in an aqueous solution and there is no aggregation of fragments and therefore no increase in molecular weight over time), from 10 days to 3 years depending on storage conditions, percent SPF, and number of shipments and shipment conditions. Additionally, pH may be altered to extend shelf life and/or support shipping conditions by preventing premature folding and aggregation of the silk. In an embodiment, the stability of the LiBr-silk fragment solution is 0 to 1 year. In an embodiment, the stability of the LiBr-silk fragment solution is 0 to 2

years. In an embodiment, the stability of the LiBr-silk fragment solution is 0 to 3 years. In an embodiment, the stability of the LiBr-silk fragment solution is 0 to 4 years. In an embodiment, the stability of the LiBr-silk fragment solution is 0 to 5 years. In an embodiment, the stability of the LiBr-silk fragment solution is 1 to 2 years. In an embodiment, the stability of the LiBr-silk fragment solution is 1 to 3 years. In an embodiment, the stability of the LiBr-silk fragment solution is 1 to 4 years. In an embodiment, the stability of the LiBr-silk fragment solution is 1 to 5 years. In an embodiment, the stability of the LiBr-silk fragment solution is 2 to 3 years. In an embodiment, the stability of the LiBr-silk fragment solution is 2 to 4 years. In an embodiment, the stability of the LiBr-silk fragment solution is 2 to 5 years. In an embodiment, the stability of the LiBr-silk fragment solution is 3 to 4 years. In an embodiment, the stability of the LiBr-silk fragment solution is 3 to 5 years. In an embodiment, the stability of the LiBr-silk fragment solution is 4 to 5 years.

In an embodiment, the stability of a composition of the present disclosure is 10 days to 6 months. In an embodiment, the stability of a composition of the present disclosure is 6 months to 12 months. In an embodiment, the stability of a composition of the present disclosure is 12 months to 18 months. In an embodiment, the stability of a composition of the present disclosure is 18 months to 24 months. In an embodiment, the stability of a composition of the present disclosure is 24 months to 30 months. In an embodiment, the stability of a composition of the present disclosure is 30 months to 36 months. In an embodiment, the stability of a composition of the present disclosure is 36 months to 48 months. In an embodiment, the stability of a composition of the present disclosure is 48 months to 60 months.

In an embodiment, a composition of the present disclosure having SPF has non-detectable levels of LiBr residuals. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is between 10 ppm and 1000 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is between 10 ppm and 300 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is less than 25 ppm. In an embodiment, the amount of the Li Br residuals in a composition of the present disclosure is less than 50 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure

is less than 75 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is less than 100 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is less than 200 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is less than 300 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is less than 400 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is less than 500 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is less than 600 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is less than 700 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is less than 800 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is less than 900 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is less than 1000 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is non-detectable to 500 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is non-detectable to 450 ppm. In an embodiment, the amount of the LiBr residue in a composition of the present disclosure is non-detectable to 400 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is non-detectable to 350 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is non-detectable to 300 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is non-detectable to 250 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is non-detectable to 200 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is non-detectable to 150 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is non-detectable to 100 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is 100 ppm to 200 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is 200 ppm to 300 ppm. In an embodiment, the amount of the LiBr residuals in a composition of the present disclosure is 300 ppm to 400 ppm. In an

embodiment, the amount of the LiBr residuals in a composition of the present disclosure is 400 ppm to 500 ppm.

In an embodiment, a composition of the present disclosure having SPF, has non-detectable levels of Na_2CO_3 residuals. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is less than 100 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is less than 200 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is less than 300 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is less than 400 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is less than 500 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is less than 600 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is less than 700 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is less than 800 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is less than 900 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is less than 1000 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is non-detectable to 500 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is non-detectable to 450 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is non-detectable to 400 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is non-detectable to 350 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is non-detectable to 300 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is non-detectable to 250 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is non-detectable to 200 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is non-detectable to 150 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is non-detectable to 100 ppm. In an

embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is 100 ppm to 200 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is 200 ppm to 300 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is 300 ppm to 400 ppm. In an embodiment, the amount of the Na_2CO_3 residuals in a composition of the present disclosure is 400 ppm to 500 ppm.

A unique feature of the SPF compositions of the present disclosure are shelf stability (they will not slowly or spontaneously gel when stored in an aqueous solution and there is no aggregation of fragments and therefore no increase in molecular weight over time), from 10 days to 3 years depending on storage conditions, percent silk, and number of shipments and shipment conditions. Additionally pH may be altered to extend shelf-life and/or support shipping conditions by preventing premature folding and aggregation of the silk. In an embodiment, a SPF solution composition of the present disclosure has a shelf stability for up to 2 weeks at room temperature (RT). In an embodiment, a SPF solution composition of the present disclosure has a shelf stability for up to 4 weeks at RT. In an embodiment, a SPF solution composition of the present disclosure has a shelf stability for up to 6 weeks at RT. In an embodiment, a SPF solution composition of the present disclosure has a shelf stability for up to 8 weeks at RT. In an embodiment, a SPF solution composition of the present disclosure has a shelf stability for up to 10 weeks at RT. In an embodiment, a SPF solution composition of the present disclosure has a shelf stability for up to 12 weeks at RT. In an embodiment, a SPF solution composition of the present disclosure has a shelf stability ranging from about 4 weeks to about 52 weeks at RT. **Table R** below shows shelf stability test results for embodiments of SPF compositions of the present disclosure.

Table R. Shelf Stability of SPF Compositions of the Present Disclosure		
% Silk	Temperature	Time to Gelation
2	RT	4 weeks
2	4 °C	>9 weeks
4	RT	4 weeks
4	4 °C	>9 weeks
6	RT	2 weeks

6	4 °C	>9 weeks
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In some embodiments, the water solubility of the silk film derived from silk fibroin protein fragments as described herein can be modified by solvent annealing (water annealing or methanol annealing), chemical crosslinking, enzyme crosslinking and heat treatment.

In some embodiments, the process of annealing may involve inducing beta-sheet formation in the silk fibroin protein fragment solutions used as a coating material. Techniques of annealing (e.g., increase crystallinity) or otherwise promoting “molecular packing” of silk fibroin-protein based fragments have been described. In some embodiments, the amorphous silk film is annealed to introduce beta-sheet in the presence of a solvent selected from the group of water or organic solvent. In some embodiments, the amorphous silk film is annealed to introduce beta-sheet in the presence of water (water annealing process). In some embodiments, the amorphous silk fibroin protein fragment film is annealed to introduce beta-sheet in the presence of methanol. In some embodiments, annealing (e.g., the beta sheet formation) is induced by addition of an organic solvent. Suitable organic solvents include, but are not limited to methanol, ethanol, acetone, isopropanol, or combination thereof.

In some embodiments, annealing is carried out by so-called “water-annealing” or “water vapor annealing” in which water vapor is used as an intermediate plasticizing agent or catalyst to promote the packing of beta-sheets. In some embodiments, the process of water annealing may be performed under vacuum. Suitable such methods have been described in Jin H-J et al. (2005), Water-stable Silk Films with Reduced Beta-Sheet Content, *Advanced Functional Materials*, 15: 1241-1247; Xiao H. et al. (2011), Regulation of Silk Material Structure by Temperature-Controlled Water Vapor Annealing, *Biomacromolecules*, 12(5): 1686-1696.

The important feature of the water annealing process is to drive the formation of crystalline beta-sheet in the silk fibroin protein fragment peptide chain to allow the silk fibroin self-assembling into a continuous film. In some embodiments, the crystallinity of the silk fibroin protein fragment film is controlled by controlling the temperature of water vapor and duration of the annealing. In some embodiments, the annealing is performed at

a temperature ranging from about 65 °C to about 110 °C. In some embodiments, the temperature of the water is maintained at about 80 °C. In some embodiments, annealing is performed at a temperature selected from the group of about 65 °C, about 70 °C, about 75 °C, about 80 °C, about 85 °C, about 90 °C, about 95 °C, about 100 °C, about 105 °C, and about 110 °C.

In some embodiments, the annealing process lasts a period of time selected from the group of about 1 minute to about 40 minutes, about 1 minute to about 50 minutes, about 1 minute to about 60 minutes, about 1 minute to about 70 minutes, about 1 minute to about 80 minutes, about 1 minute to about 90 minutes, about 1 minute to about 100 minutes, about 1 minute to about 110 minutes, about 1 minute to about 120 minutes, about 1 minute to about 130 minutes, about 5 minutes to about 40 minutes, about 5 minutes to about 50 minutes, about 5 minutes to about 60 minutes, about 5 minutes to about 70 minutes, about 5 minutes to about 80 minutes, about 5 minutes to about 90 minutes, about 5 minutes to about 100 minutes, about 5 minutes to about 110 minutes, about 5 minutes to about 120 minutes, about 5 minutes to about 130 minutes, about 10 minutes to about 40 minutes, about 10 minutes to about 50 minutes, about 10 minutes to about 60 minutes, about 10 minutes to about 70 minutes, about 10 minutes to about 80 minutes, about 10 minutes to about 90 minutes, about 10 minutes to about 100 minutes, about 10 minutes to about 110 minutes, about 10 minutes to about 120 minutes, about 10 minutes to about 130 minutes, about 15 minutes to about 40 minutes, about 15 minutes to about 50 minutes, about 15 minutes to about 60 minutes, about 15 minutes to about 70 minutes, about 15 minutes to about 80 minutes, about 15 minutes to about 90 minutes, about 15 minutes to about 100 minutes, about 15 minutes to about 110 minutes, about 15 minutes to about 120 minutes, about 15 minutes to about 130 minutes, about 20 minutes to about 40 minutes, about 20 minutes to about 50 minutes, about 20 minutes to about 60 minutes, about 20 minutes to about 70 minutes, about 20 minutes to about 80 minutes, about 20 minutes to about 90 minutes, about 20 minutes to about 100 minutes, about 20 minutes to about 110 minutes, about 20 minutes to about 120 minutes, about 20 minutes to about 130 minutes, about 25 minutes to about 40 minutes, about 25 minutes to about 50 minutes, about 25 minutes to about 60 minutes, about 25 minutes to about 70 minutes, about 25 minutes to about 80 minutes, about 25 minutes to about 90

minutes, about 25 minutes to about 100 minutes, about 25 minutes to about 110 minutes, about 25 minutes to about 120 minutes, about 25 minutes to about 130 minutes, about 30 minutes to about 40 minutes, about 30 minutes to about 50 minutes, about 30 minutes to about 60 minutes, about 30 minutes to about 70 minutes, about 30 minutes to about 80 minutes, about 30 minutes to about 90 minutes, about 30 minutes to about 100 minutes, about 30 minutes to about 110 minutes, about 30 minutes to about 120 minutes, about 30 minutes to about 130 minutes, about 35 minutes to about 40 minutes, about 35 minutes to about 50 minutes, about 35 minutes to about 60 minutes, about 35 minutes to about 70 minutes, about 35 minutes to about 80 minutes, about 35 minutes to about 90 minutes, about 35 minutes to about 100 minutes, about 35 minutes to about 110 minutes, about 35 minutes to about 120 minutes, about 35 minutes to about 130 minutes, about 40 minutes to about 50 minutes, about 40 minutes to about 60 minutes, about 40 minutes to about 70 minutes, about 40 minutes to about 80 minutes, about 40 minutes to about 90 minutes, about 40 minutes to about 100 minutes, about 40 minutes to about 110 minutes, about 40 minutes to about 120 minutes, about 40 minutes to about 130 minutes, about 45 minutes to about 50 minutes, about 45 minutes to about 60 minutes, about 45 minutes to about 70 minutes, about 45 minutes to about 80 minutes, about 45 minutes to about 90 minutes, about 45 minutes to about 100 minutes, about 45 minutes to about 110 minutes, about 45 minutes to about 120 minutes, and about 45 minutes to about 130 minutes. In some embodiments, the annealing process lasts a period of time ranging from about 1 minute to about 60 minutes. In some embodiments, the annealing process lasts a period of time ranging from about 45 minutes to about 60 minutes. The longer water annealing post-processing corresponded an increased crystallinity of silk fibroin protein fragments.

In some embodiments, the annealed silk fibroin protein fragment film is immersing the wet silk fibroin protein fragment film in 100 % methanol for 60 minutes at room temperature. The methanol annealing changed the composition of silk fibroin protein fragment film from predominantly amorphous random coil to crystalline antiparallel beta-sheet structure.

In some embodiments, the SPF as described herein can be used to prepare SPF microparticles by precipitation with methanol. Alternative flash drying, fluid-bed drying, spray drying or vacuum drying can be applied to remove water from the silk solution.

The SPF powder can then be stored and handled without refrigeration or other special handling procedures. In some embodiments, the SPF powders comprise low molecular weight silk fibroin protein fragments. In some embodiments, the SPF powders comprise mid-molecular weight silk fibroin protein fragments. In some embodiments, the SPF powders comprise a mixture of low molecular weight silk fibroin protein fragments and mid-molecular weight silk fibroin protein fragment.

In an embodiment, the water solubility of pure silk fibroin protein fragments of the present disclosure is 50 to 100%. In an embodiment, the water solubility of pure silk fibroin protein fragments of the present disclosure is 60 to 100%. In an embodiment, the water solubility of pure silk fibroin protein fragments of the present disclosure is 70 to 100%. In an embodiment, the water solubility of pure silk fibroin protein fragments of the present disclosure is 80 to 100%. In an embodiment, the water solubility is 90 to 100%. In an embodiment, the silk fibroin fragments of the present disclosure are non-soluble in aqueous solutions.

In an embodiment, the solubility of pure silk fibroin protein fragments of the present disclosure in organic solutions is 50 to 100%. In an embodiment, the solubility of pure silk fibroin protein fragments of the present disclosure in organic solutions is 60 to 100%. In an embodiment, the solubility of pure silk fibroin protein fragments of the present disclosure in organic solutions is 70 to 100%. In an embodiment, the solubility of pure silk fibroin protein fragments of the present disclosure in organic solutions is 80 to 100%. In an embodiment, the solubility of pure silk fibroin protein fragments of the present disclosure in organic solutions is 90 to 100%. In an embodiment, the silk fibroin fragments of the present disclosure are non-soluble in organic solutions.

In some embodiments, the silk fibroin protein fragments comprise cationic quaternized amino acid residue (cationic quaternized silk fibroin) with fatty alkyl groups, wherein the silk fibroin protein fragments having any weight average molecular weight and polydispersity described herein. In some embodiments, the fatty alkyl group for quaternization of amine groups of the silk fibroin protein fragment is selected from the group of cocodimonium hydroxypropyl, hydroxypropyltrimonium, laurydimonium hydroxypropyl, steardimonium hydroxypropyl, quaternium-79, and combinations thereof.

Silk Fibroin-Based Protein Fragments and Solutions Thereof

Provided herein are methods for producing pure and highly scalable SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, mixture compositions, for example solutions, that may be used to coat at least a portion of a substrate, or may be formed into usable fibers for weaving into yarn, in particular to be used with a chemical modifier, or a physical modifier. Methods of making silk fibroin or silk fibroin fragments are known and are described for example in U.S. Patents Nos. 9,187,538, 9,511,012, 9,517,191, 9,522,107, 9,522,108, 9,545,369, and 10,166,177, all of which are incorporated herein in their entireties. Methods of using silk fibroin or silk fibroin fragments in coating applications are known and are described for example in U.S. Patent Application Publications Nos. 20160222579, and 20160281294.

In some embodiments, the SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, have an average weight average molecular weight from about 1 kDa to about 5 kDa, from about 5 kDa to about 10 kDa, from about 6 kDa to about 17 kDa, from about 10 kDa to about 15 kDa, from about 15 kDa to about 20 kDa, from about 17 kDa to about 39 kDa, from about 20 kDa to about 25 kDa, from about 25 kDa to about 30 kDa, from about 30 kDa to about 35 kDa, from about 35 kDa to about 40 kDa, from about 39 kDa to about 80 kDa, from about 40 kDa to about 45 kDa, from about 45 kDa to about 50 kDa, from about 60 kDa to about 100 kDa, or from about 80 kDa to about 144 kDa, wherein the SPF and/or silk fibroin or silk fibroin fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin or silk fibroin fragments are chemically linked to a substrate through the linker. In some embodiments, the SPF as defined herein, including without limitation silk fibroin or silk fibroin fragments, have a polydispersity between 1 and about 5.0, wherein the SPF and/or silk fibroin or silk fibroin fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the SPF and/or silk fibroin or silk fibroin fragments are chemically linked to a substrate through the linker.

As used herein, “average weight average molecular weight” refers to an average of two or more values of weight average molecular weight of silk fibroin or fragments

thereof of the same compositions, the two or more values determined by two or more separate experimental readings.

As used herein, the terms “substantially sericin free” or “substantially devoid of sericin” refer to silk fibers in which a majority of the sericin protein has been removed. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 0.01% (w/w) and about 10.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 0.01% (w/w) and about 9.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 0.01% (w/w) and about 8.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 0.01% (w/w) and about 7.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 0.01% (w/w) and about 6.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 0.01% (w/w) and about 5.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 0% (w/w) and about 4.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 0.05% (w/w) and about 4.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 0.1% (w/w) and about 4.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 0.5% (w/w) and about 4.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 1.0% (w/w) and about 4.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 1.5% (w/w) and about 4.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 2.0% (w/w) and about 4.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having between about 2.5% (w/w) and about 4.0% (w/w) sericin. In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having a sericin content between about 0.01% (w/w) and about 0.1 % (w/w). In an

embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having a sericin content below about 0.1 % (w/w). In an embodiment, silk fibroin that is substantially devoid of sericin refers to silk fibroin having a sericin content below about 0.05 % (w/w). In an embodiment, when a silk source is added to a boiling (100 °C) aqueous solution of sodium carbonate for a treatment time of between about 30 minutes to about 60 minutes, a degumming loss of about 26 wt. % to about 31 wt.% is obtained.

As used herein, the term “substantially homogeneous” may refer to pure silk fibroin-based protein fragments that are distributed in a normal distribution about an identified molecular weight. As used herein, the term “substantially homogeneous” may refer to an even distribution of additive, for example vitamin C, throughout a composition of the present disclosure.

Textiles and Leathers Coated with Silk Fibroin-Based Protein Fragments

As used herein, the term “washable” and “exhibiting washability” means that a silk coated fabric of the present disclosure is capable of being washed without shrinking, fading, or the like.

As used herein, the term “textile” refers to a flexible woven or non-woven material consisting of a network of natural or artificial fibers often referred to as fabric, thread, or yarn. In an embodiment, textiles can be used to fabricate clothing, shoes and bags. In an embodiment, textiles can be used to fabricate carpeting, upholstered furnishings, window shades, towels, and coverings for tables, beds, and other flat surfaces. In an embodiment, textiles can be used to fabricate flags, backpacks, tents, nets, handkerchiefs, balloons, kites, sails, and parachutes.

As used herein, the term “leather” refers to natural leather and synthetic leather. Natural leather includes chrome-tanned leather (*e.g.*, tanned using chromium sulfate and other chromium salts), vegetable-tanned leather (*e.g.*, tanned using tannins), aldehyde-tanned leather (also known as wet-white leather, *e.g.*, tanned using glutaraldehyde or oxazolidine compounds), brain-tanned leather, formaldehyde-tanned leather, Chamois leather (*e.g.*, tanned using cod oils), rose-tanned leather (*e.g.*, tanned using rose otto oils), synthetic-tanned leather (*e.g.*, tanned using aromatic polymers), alum-tanned leather, patent leather, Vachetta leather, nubuck leather, and rawhide leather. Natural leather also includes split leather, full-grain leather, top-grain leather, and corrected-grain leather, the

properties and preparation of which are known to those of skill in the art. Synthetic leather includes poromeric imitation leathers (*e.g.*, polyurethane on polyester), vinyl and polyamide felt fibers, polyurethane, polyvinyl chloride, polyethylene (PE), polypropylene (PP), vinyl acetate copolymer (EVA), polyamide, polyester, recycled polyester, textile-polymer composite microfibers, corfan, koskin, leatherette, BIOTHANE®, BIRKIBUC®, BIRKO-FLOR®, CLARINO®, ECOLORICA®, KYDEX®, LORICA®, NAUGAHYDE®, REXINE®, VEGETAN®, FABRIKOID®, or combinations thereof.

As used herein, the term “hand” refers to the feel of a fabric, which may be further described as the feeling of softness, crispness, dryness, silkiness, and combinations thereof. Fabric hand is also referred to as “drape.” A fabric with a hard hand is coarse, rough, and generally less comfortable for the wearer. A fabric with a soft hand is fluid and smooth, such as fine silk or wool, and generally more comfortable for the wearer. Fabric hand can be determined by comparison to collections of fabric samples, or by use of methods such as the Kawabata Evaluation System (KES) or the Fabric Assurance by Simple Testing (FAST) methods. Behera and Hari, *Ind. J. Fibre & Textile Res.*, **1994**, *19*, 168-71.

As used herein, the term “yarn” refers to a single or multi-fiber construct.

As used herein, the term “bath coating” encompasses coating a fabric in a batch, immersing a fabric in a bath, and submerging a fabric in a bath. Concepts of bath coating are set forth in U.S. Patent No. 4,521,458, the entirety of which is incorporated by reference.

In an embodiment, the disclosure provides a textile or leather product coated with silk fibroin-based proteins or fragments thereof, in particular wherein the coating includes one or more chemical modifiers and/or physical modifiers. Silk fibroin coated articles have been described in U.S. Patent Application Publications Nos. 20160222579, 20160281294, and 20190003113, all of which are incorporated herein in their entireties.

In some embodiments, the article includes one or more substrates, the substrates including one or more of a fiber, a thread, a yarn, a fabric, a textile, a cloth, or a hide. In some embodiments, the fabric, textile, or cloth is woven or nonwoven. In some embodiments, the fiber, thread, or yarn includes one or more of polyester, recycled polyester, Mylar, cotton, nylon, recycled nylon, polyester-polyurethane copolymer,

rayon, acetate, aramid (aromatic polyamide), acrylic, ingeo (polylactide), lurex (polyamide-polyester), olefin (polyethylene-polypropylene), and combinations thereof. In some embodiments, the fiber, thread, or yarn includes one or more of alpaca fiber, alpaca fleece, alpaca wool, lama fiber, lama fleece, lama wool, cotton, cashmere, sheep fiber, sheep fleece, sheep wool, byssus, chiengora, qiviut, yak, rabbit, lambswool, mohair wool, camel hair, angora wool, silkworm silk, abaca fiber, coir fiber, flax fiber, jute fiber, kapok fiber, kenaf fiber, raffia fiber, bamboo fiber, hemp, modal fiber, pina, ramie, sisal, and soy protein fiber. In some embodiments, the fiber, thread, or yarn includes one or more of mineral wool, mineral cotton, man-made mineral fiber, fiberglass, glass, glasswool, stone wool, rock wool, slagwool, glass filaments, asbestos fibers, and ceramic fibers.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the SPF and/or silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the fabric exhibits an improved property, wherein the improved property is an accumulative one-way moisture transport index selected from the group consisting of greater than 40 %, greater than 60 %, greater than 80 %, greater than 100 %, greater than 120 %, greater than 140 %, greater than 160 %, and greater than 180%. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average

molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the fabric exhibits an improved property, wherein the improved property is an accumulative one way transport capability increase relative to uncoated fabric selected from the group consisting of 1.2 fold, 1.5 fold, 2.0 fold, 3.0 fold, 4.0 fold, 5.0 fold, and 10 fold. In an embodiment, the foregoing improved property is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the fabric exhibits an improved property, wherein the improved property is an overall moisture management capability selected from the group consisting of greater than 0.05, greater than 0.10, greater than 0.15, greater than 0.20, greater than 0.25, greater than 0.30, greater than 0.35, greater than 0.40, greater than 0.50, greater than 0.60, greater than 0.70, and greater than 0.80. In an embodiment, the foregoing improved property is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected

from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, and wherein the fabric exhibits substantially no increase in microbial growth after a number of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the fabric exhibits substantially no increase in microbial growth after a number of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles, and wherein the microbial growth is microbial growth of a microbe selected from the group consisting of *Staphylococcus aureus*, *Klebsiella pneumoniae*, and combinations thereof. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine

washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the fabric exhibits substantially no increase in microbial growth after a number of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles, and wherein the microbial growth is microbial growth of a microbe selected from the group consisting of *Staphylococcus aureus*, *Klebsiella pneumoniae*, and combinations thereof.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the fabric exhibits substantially no increase in microbial growth after a number of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles, wherein the microbial growth is microbial growth of a microbe selected from the group consisting of *Staphylococcus aureus*, *Klebsiella pneumoniae*, and combinations thereof, wherein the microbial growth is reduced by a percentage selected from the group consisting of 50 %, 100 %, 500 %, 1000 %, 2000 %, and 3000 % compared to an uncoated fabric.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, and wherein the coating is applied to the fabric at the fiber level prior to forming the fabric.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, and wherein the coating is applied to the fabric at the fabric level or garment level (*e.g.*, after manufacture of a garment from fabrics, leathers, and/or other materials).

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the coating is applied to the fabric at the fabric level or garment level, and wherein the fabric is bath coated.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins

or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the coating is applied to the fabric at the fabric level or garment level, and wherein the fabric is spray coated.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the coating is applied to the fabric at the fabric level or garment level, and wherein the fabric is coated with a stencil.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the coating is applied to the fabric at the fabric level or garment level, and wherein the coating is applied to at least one side of the fabric using a method selected from the group consisting of a bath coating process, a spray coating process, a stencil (*i.e.*, screen) process, a silk-foam based process, a roller-based process, a magnetic roller process, a knife process, a transfer process, a foam process, a lacquering process, and a printing process.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins

or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the coating is applied to the fabric at the fabric level, and wherein the coating is applied to both sides of the fabric using a method selected from the group consisting of a bath coating process, a spray coating process, a stencil (*i.e.*, screen) process, a silk-foam based process, a roller-based process, a magnetic roller process, a knife process, a transfer process, a foam process, a lacquering process, and a printing process.

In any of the foregoing embodiment, the coating may be applied at the fabric garment level by any of the methods disclosed herein to recondition fabrics or garments. For example, such reconditioning using a coating comprising silk based proteins or fragments thereof may be performed as part of washing or cleaning a fabric or garment.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, and wherein the coating has a thickness of about one nanolayer.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, and wherein the coating has a thickness selected from the group consisting of about 5 nm, about 10 nm, about 15 nm, about 20 nm, about 25 nm, about 50 nm, about 100 nm, about 200 nm, about 500 nm, about 1 μm , about 5 μm , about 10 μm , and about 20 μm .

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, and wherein the coating is adsorbed on the fabric.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, and wherein the coating is attached to the fabric through chemical, enzymatic, thermal, or irradiative cross-linking.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the coating is applied to the fabric at the fabric level, and wherein the hand of the coated fabric is improved relative to an uncoated fabric.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate,

and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the coating is applied to the fabric at the fabric level, and wherein the hand of the coated fabric is improved relative to an uncoated fabric, wherein the hand of the coated fabric that is improved is selected from the group consisting of softness, crispness, dryness, silkiness, and combinations thereof.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the coating is applied to the fabric at the fabric level, and wherein the pilling of the fabric is improved relative to an uncoated fabric.

In an embodiment, the silk coating is applied using a bath process, a screen (or stencil) process, a spray process, a silk-foam based process, a roller based process, a tenter frame process, or a pad-dry-cure process.

In an embodiment, a fiber or a yarn comprises a synthetic fiber or yarn, including polyester, recycled polyester, Mylar, cotton, nylon, recycled nylon, polyester-polyurethane copolymer, rayon, acetate, aramid (aromatic polyamide), acrylic, ingeo (polylactide), lurex (polyamide-polyester), olefin (polyethylene-polypropylene), and combinations thereof.

In an embodiment, a fiber or a yarn comprises a natural fiber or yarn (*e.g.*, from animal or plant sources), including alpaca fiber, alpaca fleece, alpaca wool, lama fiber, lama fleece, lama wool, cotton, cashmere and sheep fiber, sheep fleece, sheep wool, byssus, chiengora, qiviut, yak, rabbit, lambswool, mohair wool, camel hair, angora wool, silkworm silk, abaca fiber, coir fiber, flax fiber, jute fiber, kapok fiber, kenaf fiber, raffia fiber, bamboo fiber, hemp, modal fiber, pina, ramie, sisal, and soy protein fiber.

In an embodiment, a fiber or a yarn comprises a mineral fiber, also known as mineral wool, mineral cotton, or man-made mineral fiber, including fiberglass, glass,

glasswool, stone wool, rock wool, slagwool, glass filaments, asbestos fibers, and ceramic fibers.

In an embodiment, a water-soluble silk coating may be used as an adhesive or binder for binding particles to fabrics or for binding fabrics, wherein the silk based proteins or fragments in the water-soluble silk coating are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker. In an embodiment, an article comprises a fabric bound to another fabric using a silk coating. In an embodiment, an article comprises a fabric with particles bound to the fabric using a silk adhesive.

In an embodiment, the coating is applied to an article including a fabric at the yarn level. In an embodiment, the coating is applied at the fabric level. In an embodiment, the coating has a thickness selected from the group consisting of about 5 nm, about 10 nm, about 15 nm, about 20 nm, about 25 nm, about 50 nm, about 100 nm, about 200 nm, about 500 nm, about 1 μ m, about 5 μ m, about 10 μ m, and about 20 μ m. In an embodiment, the coating has a thickness range selected from the group consisting of about 5 nm to about 100 nm, about 100 nm to about 200 nm, about 200 nm to about 500 nm, about 1 μ m to about 2 μ m, about 2 μ m to about 5 μ m, about 5 μ m to about 10 μ m, and about 10 μ m to about 20 μ m.

In an embodiment, a fiber or a yarn is treated with a polymer, such as polyglycolide (PGA), polyethylene glycols, copolymers of glycolide, glycolide/L-lactide copolymers (PGA/PLLA), glycolide/trimethylene carbonate copolymers (PGA/TMC), polylactides (PLA), stereocopolymers of PLA, poly-L-lactide (PLLA), poly-DL-lactide (PDLLA), L-lactide/DL-lactide copolymers, co-polymers of PLA, lactide/tetramethylglycolide copolymers, lactide/trimethylene carbonate copolymers, lactide/ δ -valerolactone copolymers, lactide/ ϵ -caprolactone copolymers, polydepsipeptides, PLA/polyethylene oxide copolymers, unsymmetrically 3,6-substituted poly-1,4-dioxane-2,5-diones, poly- β -hydroxybutyrate (PHBA), PHBA/ β -hydroxyvalerate copolymers (PHBA/HVA), poly- β -hydroxypropionate (PHPA), poly-p-dioxanone (PDS), poly- δ -valerolactone, poly- ϵ -caprolactone, methylmethacrylate-N-vinyl pyrrolidine copolymers, polyesteramides, polyesters of oxalic acid, polydihydropyrans, polyalkyl-2-

cyanoacrylates, polyurethanes (PU), polyvinylalcohols (PVA), polypeptides, poly- β -malic acid (PMLA), poly- β -alkanoic acids, polyvinylalcohol (PVA), polyethyleneoxide (PEO), chitine polymers, polyethylene, polypropylene, polyasetal, polyamides, polyesters, recycled polyesters, polysulphone, polyether ether ketone, polyethylene terephthalate, polycarbonate, polyaryl ether ketone, and polyether ketone ketone.

In an embodiment, the silk coating surface can be modified silk crystals that range in size from nm to μm .

The criterion for “visibility” is satisfied by any one of the following: a change in the surface character of the textile; the silk coating fills the interstices where the yarns intersect; or the silk coating blurs or obscures the weave.

In an embodiment, a SPF as defined herein, for example, and without limitation, silk based protein or fragment solution may be utilized to coat at least a portion of a fabric which can be used to create a textile. In an embodiment, a silk based protein or fragment solution may be weaved into yarn that can be used as a fabric in a textile. In an embodiment, a silk based protein or fragment solution may be used to coat a fiber. In an embodiment, the disclosure provides an article comprising a silk based protein or fragment solution coating at least a portion of a fabric or a textile. In an embodiment, the disclosure provides an article comprising a silk based protein or fragment solution coating a yarn. In an embodiment, the disclosure provides an article comprising a silk based protein or fragment solution coating a fiber, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker.

There is disclosed a textile that is at least partially surface treated with an aqueous solution of SPF as defined herein, for example, and without limitation, silk fibroin-based protein fragments of the present disclosure so as to result in a silk coating on the textile, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker. In an embodiment, the silk coating of the present disclosure is available in a spray can and can be sprayed on any textile by a consumer. In an embodiment, a textile comprising a silk

coating of the present disclosure is sold to a consumer. In an embodiment, a textile of the present disclosure is used in constructing action sportswear/apparel. In an embodiment, a silk coating of the present disclosure is positioned on the underlining of apparel. In an embodiment, a silk coating of the present disclosure is positioned on the shell, the lining, or the interlining of apparel. In an embodiment, apparel is partially made from a silk coated textile of the present disclosure and partially made from an uncoated textile. In an embodiment, apparel partially made from a silk coated textile and partially made from an uncoated textile combines an uncoated inert synthetic material with a silk coated inert synthetic material. Examples of inert synthetic material include, but are not limited to, polyester, recycled polyester, polyamide, polyaramid, polytetrafluoroethylene, polyethylene, polypropylene, polyurethane, silicone, mixtures of polyurethane and polyethyleneglycol, ultrahigh molecular weight polyethylene, high-performance polyethylene, and mixtures thereof. In an embodiment, apparel partially made from a silk coated textile and partially made from an uncoated textile combines an elastomeric material at least partially covered with a silk coating of the present disclosure. In an embodiment, the percentage of silk to elastomeric material can be varied to achieve desired shrink or wrinkle resistant properties.

In an embodiment, a silk coating of the present disclosure is visible. In an embodiment, a silk coating of the present disclosure positioned on apparel helps control skin temperature. In an embodiment, a silk coating of the present disclosure positioned on apparel helps control fluid transfer away from the skin. In an embodiment, a silk coating of the present disclosure positioned on apparel has a soft feel against the skin decreasing abrasions from fabric on skin. In an embodiment, a silk coating of the present disclosure positioned on a textile has properties that confer at least one of wrinkle resistance, shrinkage resistance, or machine washability to the textile. In an embodiment, a silk coated textile of the present disclosure is 100% machine washable and dry cleanable. In an embodiment, a silk coated textile of the present disclosure is 100% waterproof. In an embodiment, a silk coated textile of the present disclosure is wrinkle resistant. In an embodiment, a silk coated textile of the present disclosure is shrink resistant. In an embodiment, a silk coated textile of the present disclosure has the qualities of being waterproof, breathable, and elastic and possess a number of other qualities which are

highly desirable in action sportswear. In an embodiment, a silk coated textile of the present disclosure manufactured from a silk fabric of the present disclosure further includes LYCRA® brand spandex fibers.

In an embodiment, a textile at least partially coated with an aqueous solution of SPF as defined herein, for example, and without limitation, silk fibroin-based protein fragments of the present disclosure is a breathable fabric. In an embodiment, a textile at least partially coated with an aqueous solution of SPF as defined herein, for example, and without limitation, silk fibroin-based protein fragments of the present disclosure is a water-resistant fabric. In an embodiment, a textile at least partially coated with an aqueous solution of SPF as defined herein, for example, and without limitation, silk fibroin-based protein fragments of the present disclosure is a shrink-resistant fabric. In an embodiment, a textile at least partially coated with an aqueous solution of SPF as defined herein, for example, and without limitation, silk fibroin-based protein fragments of the present disclosure is a machine-washable fabric. In an embodiment, a textile at least partially coated with an aqueous solution of SPF as defined herein, for example, and without limitation, silk fibroin-based protein fragments of the present disclosure is a wrinkle resistant fabric. In an embodiment, textile at least partially coated with an aqueous solution of SPF as defined herein, for example, and without limitation, silk fibroin-based protein fragments of the present disclosure provides moisture and vitamins to the skin.

In an embodiment, an aqueous solution of SPF as defined herein, for example, and without limitation, silk fibroin-based protein fragments of the present disclosure is used to coat a textile or leather, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate. In an embodiment, the concentration of silk in the solution ranges from about 0.1% to about 20.0%. In an embodiment, the concentration of silk in the solution ranges from about 0.1% to about 15.0%. In an embodiment, the concentration of silk in the solution ranges from about 0.5% to about 10.0%. In an embodiment, the concentration of silk in the solution ranges from about 1.0% to about 5.0%. In an embodiment, an aqueous solution of pure silk fibroin-based protein fragments of the present disclosure is applied directly to a fabric. Alternatively, silk microsphere and any additives may be used for coating a fabric. In an

embodiment, additives can be added to an aqueous solution of pure silk fibroin-based protein fragments of the present disclosure before coating (*e.g.*, alcohols) to further enhance material properties. In an embodiment, a silk coating of the present disclosure can have a pattern to optimize properties of the silk on the fabric. In an embodiment, a coating is applied to a fabric under tension and/or lax to vary penetration in to the fabric.

In an embodiment, a silk coating of the present disclosure can be applied at the yarn level, followed by creation of a fabric once the yarn is coated. In an embodiment, an aqueous solution of pure silk fibroin-based protein fragments of the present disclosure can be spun into fibers to make a silk fabric and/or silk fabric blend with other materials known in the apparel industry.

Uses of Textiles and Leathers Coated with Silk Fibroin-Based Protein Fragments in Apparel and Garment Applications

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article exhibits an improved color retention property. Without being bound by any specific theory, it is postulated that the coating prevents the article from color degradation by separating the fiber or yarn from air or from detergents during washing.

Methods of testing the color retention property of an article are well within the knowledge of one skilled in the art. A specific method of testing of the color retention property of a fabric is described in U.S. Patent No. 5,142,292, which is incorporated herein by reference in its entirety.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate,

and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article exhibits an improved color retention property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article exhibits an improved color retention property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the article exhibits an improved color retention property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins

or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article exhibits an improved color retention property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article exhibits an improved color retention property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the article exhibits an improved color retention property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the article exhibits an improved color retention property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, wherein the article exhibits an improved color retention property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric,

wherein the article exhibits an improved color retention property. In an embodiment, the foregoing color retention property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits an improved color retention property. In an embodiment, the foregoing improved color retention property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is resistant to microbial (including bacterial and fungal) growth.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins

or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is resistant to microbial (including bacterial and fungal) growth.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article is resistant to microbial (including bacterial and fungal) growth.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the article is resistant to microbial (including bacterial and fungal) growth.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are

chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article is resistant to microbial (including bacterial and fungal) growth.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article is resistant to microbial (including bacterial and fungal) growth.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins

or fragments comprise silk and a copolymer, wherein the article is resistant to microbial (including bacterial and fungal) growth.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the article is resistant to microbial (including bacterial and fungal) growth.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, wherein the article is resistant to microbial (including bacterial and fungal) growth.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate,

and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is resistant to microbial (including bacterial and fungal) growth. In an embodiment, the foregoing resistant to microbial (including bacterial and fungal) growth property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits resistant to microbial (including bacterial and fungal) growth property. In an embodiment, the foregoing resistant to microbial (including bacterial and fungal) growth property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is resistant to the buildup of static electrical charge.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is resistant to the buildup of static electrical charge.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article is resistant to the buildup of static electrical charge.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the article is resistant to the buildup of static electrical charge.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and

without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article is resistant to the buildup of static electrical charge.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article is resistant to the buildup of static electrical charge.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average

molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the article is resistant to the buildup of static electrical charge.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the article is resistant to the buildup of static electrical charge.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, wherein the article is resistant to the buildup of static electrical charge.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is resistant to the buildup of static electrical charge. In an embodiment, the foregoing resistant to the buildup of static electrical charge property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits resistant to the buildup of static electrical charge property. In an embodiment, the foregoing resistant to the buildup of static electrical charge property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is mildew resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and

without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is mildew resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article is mildew resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the article is mildew resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are

chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article is mildew resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article is mildew resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the article is mildew resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the article is mildew resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, wherein the article is mildew resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric,

wherein the article is mildew resistant. In an embodiment, the foregoing mildew resistant property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits mildew resistant property. In an embodiment, the foregoing mildew resistant property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the coating is transparent.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins

or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the coating is transparent.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the coating is transparent.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the coating is transparent.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins

or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the coating is transparent.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the coating is transparent.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the coating is transparent.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and

without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the coating is transparent.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, wherein the coating is transparent.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the coating is transparent. In an embodiment, the foregoing transparent property of the coating is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the

foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather comprises a silk coating of the present disclosure, wherein the silk coating is transparent. In an embodiment, the foregoing transparent property of the coating is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is resistant to freeze-thaw cycle damage.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are

chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is resistant to freeze-thaw cycle damage.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article is resistant to freeze-thaw cycle damage.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the article is resistant to freeze-thaw cycle damage.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and

combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article is resistant to freeze-thaw cycle damage.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article is resistant to freeze-thaw cycle damage.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the article is resistant to freeze-thaw cycle damage.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the article is resistant to freeze-thaw cycle damage.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, wherein the article is resistant to freeze-thaw cycle damage.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric,

wherein the article is resistant to freeze-thaw cycle damage. In an embodiment, the foregoing resistant to freeze-thaw cycle damage property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits resistant to freeze-thaw cycle damage. In an embodiment, the foregoing resistant to freeze-thaw cycle damage property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the coating provides protection from abrasion.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are

chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the coating provides protection from abrasion.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the coating provides protection from abrasion.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the coating provides protection from abrasion.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and

combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the coating provides protection from abrasion.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the coating provides protection from abrasion.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the coating provides protection from abrasion.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and

without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the coating provides protection from abrasion.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, wherein the coating provides protection from abrasion.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the coating provides protection from abrasion. In an embodiment, the foregoing abrasion resistant property of the fabric is determined after a period of machine washing

cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits abrasion resistant. In an embodiment, the foregoing abrasion resistant property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article exhibits the property of blocking ultraviolet (UV) radiation.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are

chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article exhibits the property of blocking ultraviolet (UV) radiation.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article exhibits the property of blocking ultraviolet (UV) radiation.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the article exhibits the property of blocking ultraviolet (UV) radiation.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins

or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article exhibits the property of blocking ultraviolet (UV) radiation.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article exhibits the property of blocking ultraviolet (UV) radiation.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the article exhibits the property of blocking ultraviolet (UV) radiation.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the article exhibits the property of blocking ultraviolet (UV) radiation.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, wherein the article exhibits the property of blocking ultraviolet (UV) radiation.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric,

wherein the article exhibits the property of blocking ultraviolet (UV) radiation. In an embodiment, the foregoing UV blocking property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits UV blocking property. In an embodiment, the foregoing UV blocking property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides a garment comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the garment regulates the body temperature of a wearer.

In an embodiment, the disclosure provides a garment comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins

or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the garment regulates the body temperature of a wearer.

In an embodiment, the disclosure provides a garment comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the garment regulates the body temperature of a wearer.

In an embodiment, the disclosure provides a garment comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the garment regulates the body temperature of a wearer.

In an embodiment, the disclosure provides a garment comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins

or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the garment regulates the body temperature of a wearer.

In an embodiment, the disclosure provides a garment comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the garment regulates the body temperature of a wearer.

In an embodiment, the disclosure provides a garment comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins

or fragments comprise silk and a copolymer, wherein the garment regulates the body temperature of a wearer.

In an embodiment, the disclosure provides a garment comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the garment regulates the body temperature of a wearer.

In an embodiment, the disclosure provides a garment comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, wherein the garment regulates the body temperature of a wearer.

In an embodiment, the disclosure provides a garment comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate,

and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the garment regulates the body temperature of a wearer. In an embodiment, the foregoing temperature regulation property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits a temperature regulation property. In an embodiment, the foregoing temperature regulation property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, and wherein the article is tear resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and

without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, and wherein the article is tear resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, and wherein the article is tear resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, and wherein the article is tear resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are

chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, and wherein the article is tear resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, and wherein the article is tear resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, and wherein the article is tear resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, and wherein the article is tear resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, and wherein the article is tear resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric,

and wherein the article is tear resistant. In an embodiment, the foregoing tear resistant property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits a tear resistant property. In an embodiment, the foregoing tear resistant property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the elasticity of the article is improved.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate,

and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the elasticity of the article is reduced.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the elasticity of the article is improved.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the elasticity of the article is reduced.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article exhibits a rebound dampening property. Without being bound by any specific theory, it is

postulated that the coating prevents the article from returning to the original shape or orientation, and results in the rebound dampening property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article exhibits a rebound dampening property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article exhibits a rebound dampening property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the article exhibits a rebound dampening property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article exhibits a rebound dampening property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article exhibits a rebound dampening property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the article exhibits a rebound dampening property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the article exhibits a rebound dampening property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-

polyurethane copolymer, and combinations thereof, wherein the article exhibits a rebound dampening property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article exhibits a rebound dampening property. In an embodiment, the foregoing rebound dampening property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits a rebound dampening property. In an embodiment, the foregoing rebound dampening property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average

molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article exhibits an anti-itch property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article exhibits an anti-itch property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article exhibits an anti-itch property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins

or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the article exhibits an anti-itch property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article exhibits an anti-itch property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article exhibits an anti-itch property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the article exhibits an anti-itch property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the article exhibits an anti-itch property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-

polyurethane copolymer, and combinations thereof, wherein the article exhibits an anti-itch property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article exhibits an anti-itch property. In an embodiment, the foregoing anti-itch property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits an anti-itch property. In an embodiment, the foregoing anti-itch property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins

or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article exhibits an improved insulation/warmth property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article exhibits an improved insulation/warmth property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article exhibits an improved insulation/warmth property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and

combinations thereof, wherein the article exhibits an improved insulation/warmth property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article exhibits an improved insulation/warmth property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based

proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article exhibits an improved insulation/warmth property.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article exhibits an improved insulation/warmth property. In an embodiment, the foregoing improved insulation/warmth property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits improved an insulation/warmth property. In an embodiment, the foregoing improved insulation/warmth property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average

molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is wrinkle resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is wrinkle resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article is wrinkle resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins

or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the article is wrinkle resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article is wrinkle resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article is wrinkle resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the article is wrinkle resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the article is wrinkle resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-

polyurethane copolymer, and combinations thereof, wherein the article is wrinkle resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is wrinkle resistant. In an embodiment, the foregoing wrinkle resistant property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits wrinkle resistant property. In an embodiment, the foregoing wrinkle resistant property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average

molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is stain resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is stain resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article is stain resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins

or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the article is stain resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article is stain resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article is stain resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the article is stain resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the article is stain resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, wherein the article is stain resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is stain resistant. In an embodiment, the foregoing stain resistant property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits stain resistant property. In an embodiment, the foregoing stain resistant property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate,

and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is sticky. Without being bound to any specific theory, it is postulated that the coating provides stickiness and maintains stickiness.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is sticky.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article is sticky.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is sticky. In an embodiment, the foregoing sticky property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the

foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure exhibits sticky property. In an embodiment, the foregoing sticky property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides an article comprising a textile or leather coated with silk fibroin-based proteins or fragments thereof, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article exhibits improved flame resistance relative to an uncoated textile. In an embodiment, the disclosure provides an article comprising a textile or leather coated with silk fibroin-based proteins or fragments thereof, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article exhibits equal flame resistance relative to an uncoated textile or leather. In an embodiment, the disclosure provides an article comprising a textile or leather coated with silk fibroin-based proteins or fragments thereof, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the

linker, wherein the article exhibits equal flame resistance relative to an uncoated textile or leather, wherein an alternative textile or leather coating exhibits reduced flame resistance. In an embodiment, the disclosure provides an article comprising a textile or leather coated with silk fibroin-based proteins or fragments thereof, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article exhibits improved resistance to fire relative to an uncoated textile or leather, wherein the improved resistance to fire is determined by a flammability test. In an embodiment, the flammability test measures afterflame time, afterglow time, char length, and the observation of fabric melting or dripping.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is flame resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the article is flame resistant.

In an embodiment, the disclosure provides an article comprising a polyester having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins

or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is flame resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof comprise silk fibroin-based proteins or protein fragments having about 0.01% (w/w) to about 10% (w/w) sericin, wherein the article is flame resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the article is flame resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins

or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the article is flame resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments thereof are selected from the group consisting of natural silk based proteins or fragments thereof, recombinant silk based proteins or fragments thereof, and combinations thereof, wherein the silk based proteins or fragments thereof are natural silk based proteins or fragments thereof that are selected from the group consisting of spider silk based proteins or fragments thereof, silkworm silk based proteins or fragments thereof, and combinations thereof, wherein the natural silk based proteins or fragments are silkworm silk based proteins or fragments thereof, and the silkworm silk based proteins or fragments thereof is *Bombyx mori* silk based proteins or fragments thereof, wherein the article is flame resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the silk based proteins or fragments comprise silk and a copolymer, wherein the article is flame resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and

without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is natural fiber or yarn selected from the group consisting of cotton, alpaca fleece, alpaca wool, lama fleece, lama wool, cotton, cashmere, sheep fleece, sheep wool, and combinations thereof, wherein the article is flame resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the fiber or yarn is selected from the group consisting of natural fiber or yarn, synthetic fiber or yarn, or combinations thereof, wherein the fiber or yarn is synthetic fiber or yarn selected from the group consisting of polyester, recycled polyester, nylon, recycled nylon, polyester-polyurethane copolymer, and combinations thereof, wherein the article is flame resistant.

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, wherein the fabric is flame resistant. In an embodiment, the foregoing flame resistant property of the fabric is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an

embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, a textile or leather of the present disclosure is flame resistant. In an embodiment, the foregoing flame resistant property of the textile is determined after a period of machine washing cycles selected from the group consisting of 5 cycles, 10 cycles, 25 cycles, and 50 cycles. In an embodiment, the foregoing improved property, or any other improved property described herein, is determined after a period of machine washing (e.g., by home laundering machine washing) cycles selected from the group consisting of 0 cycles, 1 cycle, 2 cycles, 3 cycles, 4 cycles, 5 cycles, 6 cycles, 7 cycles, 8 cycles, 9 cycles, 10 cycles, 11 cycles, 12 cycles, 13 cycles, 14 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles, 35 cycles, 40 cycles, 45 cycles, and 50 cycles.

In an embodiment, the disclosure provides a leather coated with coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the leather exhibits an property selected from the group consisting of an improved color retention property, improved mildew resistance, improved resistance to freeze-thaw cycle damage, improved resistance to abrasion, improved blocking of ultraviolet (UV) radiation, improved regulation of the body temperature of a wearer, improved tear resistance, improved elasticity, improved rebound dampening, improved anti-itch properties, improved insulation, improved wrinkle resistance, improved stain resistance, and improved stickiness. In an embodiment, the disclosure provides a leather coated with coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to

about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the coating is transparent.

In any of the foregoing embodiments, at least one property of the article is improved, wherein the property that is improved is selected from the group consisting of color retention, resistance to microbial growth, resistance to bacterial growth, resistance to fungal growth, resistance to the buildup of static electrical charge, resistance to the growth of mildew, transparency of the coating, resistance to freeze-thaw cycle damage, resistance from abrasion, blocking of ultraviolet (UV) radiation, regulation of the body temperature of a wearer, resistance to tearing, elasticity of the article, rebound dampening, tendency to cause itching in the wearer, thermal insulation of the wearer, wrinkle resistance, stain resistance, stickiness to skin, and flame resistance, and wherein the property is improved by an amount relative to an uncoated article selected from the group consisting of at least 5%, at least 10%, at least 15%, at least 20%, at least 25%, at least 30%, at least 35%, at least 40%, at least 45%, at least 50%, at least 55%, at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, at least 100%, at least 125%, at least 150%, at least 200%, at least 300%, at least 400%, and at least 500%.

In any of the foregoing embodiments, the silk based proteins or protein fragments thereof have an average weight average molecular weight range selected from the group consisting of about 5 to about 10 kDa, about 6 kDa to about 16 kDa, about 17 kDa to about 38 kDa, about 39 kDa to about 80 kDa, about 60 to about 100 kDa, and about 80 kDa to about 144 kDa, wherein the silk based proteins or fragments thereof have a polydispersity of between about 1.5 and about 3.0, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to a fiber or yarn through the linker, and optionally wherein the proteins or protein fragments, prior to coating the fabric, do not spontaneously or gradually gelate and do not visibly change in color or turbidity when in a solution for at least 10 days.

Additional Agents for Use with Textiles Coated with Silk Fibroin-Based Protein

Fragments

In an embodiment, the disclosure provides an article comprising a fiber or yarn having a coating, wherein the coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the fiber or yarn through the linker, wherein the article is a fabric, and wherein the fabric is pretreated with various additional agents. Additional agents are described in U.S. Patent Application Publications Nos. 20160222579, 20160281294, and 20190003113, all of which are incorporated herein in their entireties.

Other Materials Coated with Silk Fibroin-Based Protein Fragments

In an embodiment, the disclosure provides a material coated with silk fibroin-based proteins or fragments thereof. The material may be any material suitable for coating, including plastics (*e.g.*, vinyl), foams (*e.g.*, for use in padding and cushioning), and various natural or synthetic products.

In an embodiment, the disclosure provides an automobile component coated with silk fibroin-based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the component through the linker. In an embodiment, the disclosure provides an automobile component coated with silk fibroin-based proteins or fragments thereof having a weight average molecular weight range selected from the group consisting of about 5 to about 10 kDa, about 6 kDa to about 16 kDa, about 17 kDa to about 38 kDa, about 39 kDa to about 80 kDa, about 60 to about 100 kDa, and about 80 kDa to about 144 kDa, wherein the silk based proteins or fragments thereof have a polydispersity of between about 1.5 and about 3.0, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to

the component through the linker, and optionally wherein the proteins or protein fragments, prior to coating the fabric, do not spontaneously or gradually gelate and do not visibly change in color or turbidity when in a solution for at least 10 days. In an embodiment, the disclosure provides an automobile component coated with silk fibroin-based proteins or fragments thereof, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the component through the linker, wherein the automobile component exhibits an improved property relative to an uncoated automobile component. In an embodiment, the disclosure provides an automobile component coated with silk fibroin-based proteins or fragments thereof, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the component through the linker, wherein the automobile component exhibits an improved property relative to an uncoated automobile component, and wherein the automobile component is selected from the group consisting of an upholstery fabric, a headliner, a seat, a headrest, a transmission control, a floor mat, a carpet fabric, a dashboard, a steering wheel, a trim, a wiring harness, an airbag cover, an airbag, a sunvisor, a seat belt, a headrest, an armrest, and a children's car seat. In an embodiment, the disclosure provides an electrical component insulated with a coating comprising silk fibroin-based proteins or fragments thereof, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the component through the linker,.

In an embodiment, the disclosure provides a foam coated with silk fibroin-based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the foam through the linker. In an embodiment, the disclosure provides a foam coated with silk fibroin-based proteins or fragments thereof having a weight average molecular

weight range selected from the group consisting of about 5 to about 10 kDa, about 6 kDa to about 16 kDa, about 17 kDa to about 38 kDa, about 39 kDa to about 80 kDa, about 60 to about 100 kDa, and about 80 kDa to about 144 kDa, wherein the silk based proteins or fragments thereof have a polydispersity of between about 1.5 and about 3.0, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the foam through the linker, and optionally wherein the proteins or protein fragments, prior to coating the foam, do not spontaneously or gradually gelate and do not visibly change in color or turbidity when in a solution for at least 10 days. In an embodiment, the disclosure provides a foam coated with silk fibroin-based proteins or fragments thereof, wherein the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to the foam through the linker, wherein the foam exhibits an improved property relative to an uncoated foam, and wherein the foam is selected from the group consisting of a polyurethane foam, an ethylene-vinyl acetate copolymer foam, a low density polyethylene foam, a low density polyethylene foam, a high density polyethylene foam, a polypropylene copolymer foam, a linear low density polyethylene foam, a natural rubber foam, a latex foam, and combinations thereof.

In any of the foregoing embodiments, the material coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 5 kDa to about 144 kDa. In any of the foregoing embodiments, the material coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 6 kDa to about 16 kDa. In any of the foregoing embodiments, the material coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 17 kDa to about 38 kDa. In any of the foregoing embodiments, the material coating comprises SPF as defined herein, for example, and without limitation, silk based proteins or fragments thereof having a weight average molecular weight range of about 39 kDa to about 80 kDa. In any of the foregoing

embodiments, the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to a substrate through the linker.

In any of the foregoing embodiments, the silk based proteins or protein fragments thereof have an average weight average molecular weight range selected from the group consisting of about 5 to about 10 kDa, about 6 kDa to about 16 kDa, about 17 kDa to about 38 kDa, about 39 kDa to about 80 kDa, about 60 to about 100 kDa, and about 80 kDa to about 144 kDa, wherein the silk based proteins or fragments thereof have a polydispersity of between about 1.5 and about 3.0, the silk based proteins or fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk based proteins or fragments thereof are chemically linked to a substrate through the linker, and wherein the proteins or protein fragments, prior to coating the fabric, do not spontaneously or gradually gelate and do not visibly change in color or turbidity when in a solution for at least 10 days.

Processes for Coating Textiles and Leathers with Silk Fibroin-Based Protein Fragments

In an embodiment, a method for silk coating a textile, leather, or other material (such as a foam) includes immersion of the textile, leather, or other material in any of the aqueous solutions of pure silk fibroin-based protein fragments of the present disclosure. Such methods are described in U.S. Patent Application Publications Nos. 20160222579, 20160281294, and 20190003113, all of which are incorporated herein in their entireties. In some embodiments, the disclosure relates to such methods including the use of chemical modifiers and/or physical modifiers. In an embodiment, a method for silk coating a textile, leather, or other material (such as a foam) includes chemically modifying silk based proteins or fragments with a precursor linker to form a silk-conjugate, and optionally chemically linking the silk based proteins or fragments thereof to a substrate through the linker.

Additives for Silk Fibroin-Based Protein Fragments and Solutions Thereof

In an embodiment, a solution of the present disclosure is contacted with an additive, such as a therapeutic agent and/or an additive molecule. U.S. Patent Application Publications Nos. 20160222579, 20160281294, and 20190003113, all of which are

incorporated herein in their entireties. The present disclosure relates in particular to the use of such solutions, therapeutic agents, and/or additive molecules in conjunction with a chemical modifier and/or physical modifier.

Processes for Production of Silk Fibroin-Based Protein Fragments and Solutions Thereof

As used herein, the term “fibroin” includes silkworm fibroin and insect or spider silk protein. In an embodiment, fibroin is obtained from *Bombyx mori*. In an embodiment, the spider silk protein is selected from the group consisting of swathing silk (Achniform gland silk), egg sac silk (Cylindriform gland silk), egg case silk (Tubuliform silk), non-sticky dragline silk (Ampullate gland silk), attaching thread silk (Pyriform gland silk), sticky silk core fibers (Flagelliform gland silk), and sticky silk outer fibers (Aggregate gland silk). Methods of making silk fibroin or silk fibroin fragments are known and are described for example in U.S. Patents Nos. 9,187,538, 9,511,012, 9,517,191, 9,522,107, 9,522,108, 9,545,369, and 10,166,177, and U.S. Patent Application Publications Nos. 20160222579, 20160281294, and 20190003113, all of which are incorporated herein in their entireties.

In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 6 kDa to about 17 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 17 kDa to about 39 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 39 kDa to about 80 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker.

In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 1 kDa to about 5 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 5 kDa to about 10 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 10 kDa to about 15 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 15 kDa to about 20 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 20 kDa to about 25 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 25 kDa to about 30 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically

linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 30 kDa to about 35 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 35 to about 40 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 40 to about 45 kDa. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 45 to about 50 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker.

In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 50 to about 55 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 55 to about 60 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight

average molecular weight ranging from about 60 to about 65 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 65 to about 70 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 70 to about 75 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 75 to about 80 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 80 to about 85 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 85 to about 90 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an

average weight average molecular weight ranging from about 90 to about 95 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 95 to about 100 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker.

In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 100 to about 105 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 105 to about 110 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 110 to about 115 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 115 to about 120 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In

an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 120 to about 125 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 125 to about 130 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 130 to about 135 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 135 to about 140 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 140 to about 145 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 145 to about 150 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the

silk fibroin-based protein fragments are chemically linked to a substrate through the linker.

In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 150 to about 155 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 155 to about 160 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 160 to about 165 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 165 to about 170 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 170 to about 175 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 175 to about 180 kDa, wherein the silk fibroin-based protein fragments are

chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 180 to about 185 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 185 to about 190 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 190 to about 195 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 195 to about 200 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker.

In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 200 to about 205 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average

molecular weight ranging from about 205 to about 210 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 210 to about 215 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 215 to about 220 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 220 to about 225 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 225 to about 230 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 230 to about 235 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight

average molecular weight ranging from about 235 to about 240 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 240 to about 245 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 245 to about 250 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker.

In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 250 to about 255 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 255 to about 260 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 260 to about 265 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a

coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 265 to about 270 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 270 to about 275 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 275 to about 280 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 280 to about 285 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 285 to about 290 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 290 to about 295 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In

an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 295 to about 300 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker.

In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 300 to about 305 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 305 to about 310 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 310 to about 315 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 315 to about 320 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 320 to about 325 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the

silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 325 to about 330 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 330 to about 335 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 335 to about 340 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 340 to about 345 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a coating of the present disclosure includes silk fibroin-based protein fragments having an average weight average molecular weight ranging from about 345 to about 350 kDa, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker.

In an embodiment, a composition of the present disclosure, for example a coating or a composition used to make such coating, includes silk fibroin-based protein fragments having a polydispersity ranging from about 1 to about 5.0, wherein the silk fibroin-based

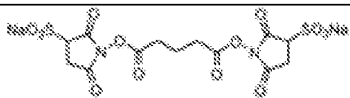
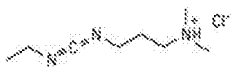
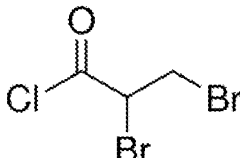
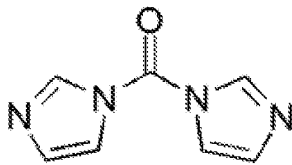
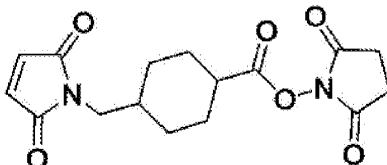
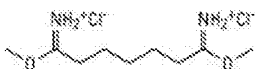
protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a composition of the present disclosure, for example a coating or a composition used to make such coating, includes silk fibroin-based protein fragments having a polydispersity ranging from about 1.5 to about 3.0, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a composition of the present disclosure, for example a coating or a composition used to make such coating, includes silk fibroin-based protein fragments having a polydispersity ranging from about 1 to about 1.5, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a composition of the present disclosure, for example a coating or a composition used to make such coating, includes silk fibroin-based protein fragments having a polydispersity ranging from about 1.5 to about 2.0, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a composition of the present disclosure, for example a coating or a composition used to make such coating, includes silk fibroin-based protein fragments having a polydispersity ranging from about 2.0 to about 2.5, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In an embodiment, a composition of the present disclosure, for example a coating or a composition used to make such coating, includes silk fibroin-based protein fragments having a polydispersity ranging from about 2.0 to about 3.0, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker. In

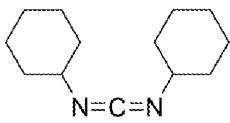
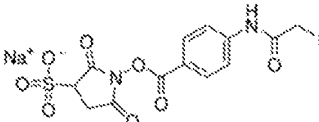
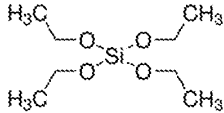
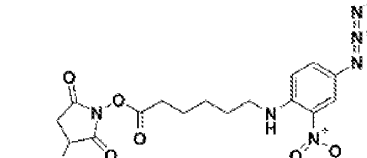
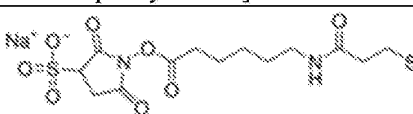
an embodiment, a composition of the present disclosure, for example a coating or a composition used to make such coating, includes silk fibroin-based protein fragments having a polydispersity ranging from about 2.5 to about 3.0, wherein the silk fibroin-based protein fragments are chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin-based protein fragments are chemically linked to a substrate through the linker.

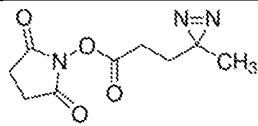
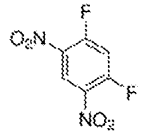
Chemical Modification of Silk Fibroin

The disclosure relates to articles including one or more coated substrates, wherein the coatings include silk fibroin or silk fibroin fragments and a chemical modifier or a physical modifier. In some embodiments, the chemical modifier is chemically linked to one or more of a silk fibroin side group and a silk fibroin terminal group. In some embodiments, the silk fibroin side group and the silk fibroin terminal group are independently selected from an amine group, an amide group, a carboxyl group, a hydroxyl group, a thiol group, and a sulfhydryl group. In some embodiments, the chemical modifier is chemically linked to one or more functional groups on the substrate. In some embodiments, the functional group on the substrate is selected from an amine group, an amide group, a carboxyl group, a hydroxyl group, a thiol group, and a sulfhydryl group. In some embodiments, the chemical modifier includes one or more of a chemically linked functional group, or functional group residue, and a linker. In some embodiments, the chemical modifier includes one or more of $-\text{CR}^a_2-$, $-\text{CR}^a=\text{CR}^a-$, $-\text{C}\equiv\text{C}-$, $-\text{alkyl}-$, $-\text{alkenyl}-$, $-\text{alkynyl}-$, $-\text{aryl}-$, $-\text{heteroaryl}-$, $-\text{O}-$, $-\text{S}-$, $-\text{OC}(\text{O})-$, $-\text{N}(\text{R}^a)-$, $-\text{N}=\text{N}-$, $=\text{N}-$, $-\text{C}(\text{O})-$, $-\text{C}(\text{O})\text{O}-$, $-\text{OC}(\text{O})\text{N}(\text{R}^a)-$, $-\text{C}(\text{O})\text{N}(\text{R}^a)-$, $-\text{N}(\text{R}^a)\text{C}(\text{O})\text{O}-$, $-\text{N}(\text{R}^a)\text{C}(\text{O})-$, $-\text{N}(\text{R}^a)\text{C}(\text{O})\text{N}(\text{R}^a)-$, $-\text{N}(\text{R}^a)\text{C}(\text{NR}^a)\text{N}(\text{R}^a)-$, $-\text{N}(\text{R}^a)\text{S}(\text{O})_t-$, $-\text{S}(\text{O})_t\text{O}-$, $-\text{S}(\text{O})_t\text{N}(\text{R}^a)-$, $-\text{S}(\text{O})_t\text{N}(\text{R}^a)\text{C}(\text{O})-$, $-\text{OP}(\text{O})(\text{OR}^a)\text{O}-$, wherein t is 1 or 2, and wherein at each independent occurrence R^a is selected from hydrogen, alkyl, alkenyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl, or heteroarylalkyl.

In some embodiments, any SPF described herein, including silk fibroin or silk fibroin-based protein fragments are chemically modified with a precursor linker to form silk conjugates. Precursor linkers can be selected from any of the following crosslinkers:

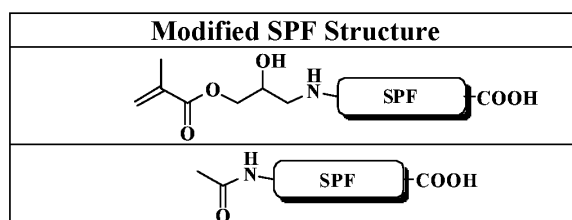
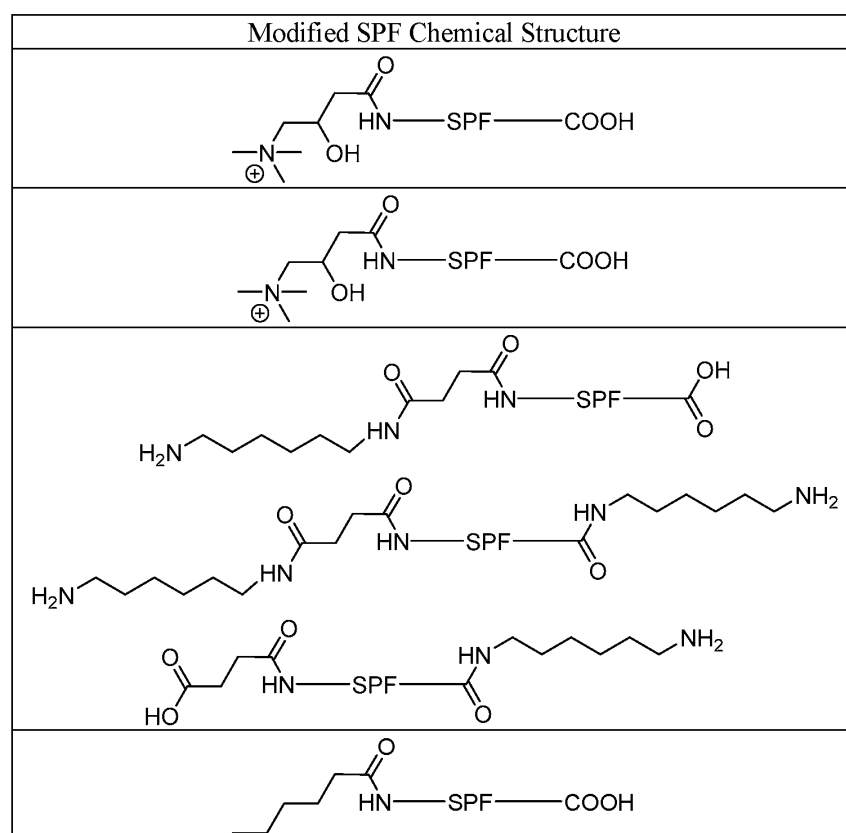
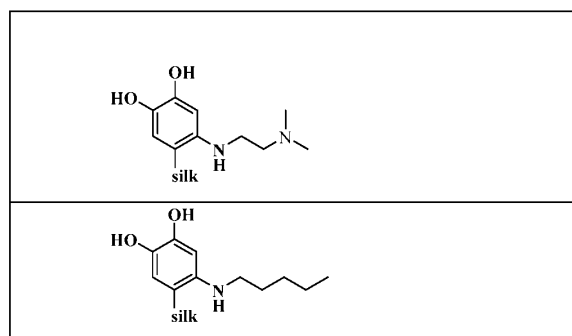
Class of Crosslinker	Example of chemical group reactivity	Example
Succinimidyl	Amine	 Bis[Sulfosuccinimidyl] glutarate
Carbodiimide	Carboxyls	 EDC 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide • HCl MW 391.70 Spacer Arm 6.0 Å
Acyl chloride	Amines/Hydroxyls	 2,3-Dibromopropionyl chloride
Carbonyldiimidazole	Amine/Hydroxyls	 N,N'-Carbonyldiimidazole
NHS-maleimide crosslinking,	Thiol	 Succinimidyl-4-[N-maleimidomethyl]cyclohexane-1-carboxylate
Imidoester crosslinking	Amine	 DMP dimethyl pimelimidate

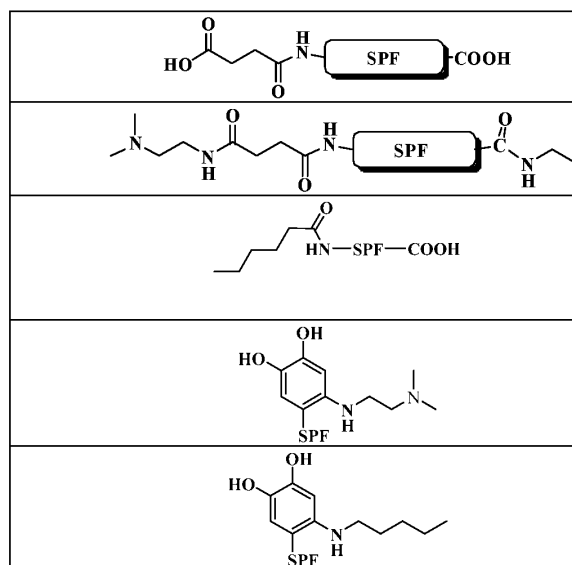
dicyclohexyl carbodiimide crosslinking	Amines	
NHS-haloacetyl crosslinking Sulfo-SIAB (sulfosuccinimidyl (4-iodoacetyl)aminobenzoate)	Amine	
Methacrylate		
Epoxide	Hydroxyl/amines	
Silanes	Hydroxyls	 TEOS Tetraethyl orthosilicate
Alkyne- Click Chemistry	Azide	
Azide-click Chemistry	Alkyne	
Aldehyde	Amines	
Formaldehyde	Amines	
Thioester	Thiols, amines, hydroxyls	
Photo-crosslinker	Amines	 N-Sulfosuccinimidyl-6-[4'-azido-2'-nitrophenylamino] hexanoate
pyridyl thiol, sulfosuccinimidyl 6-[3'-(2-pyridyldithio)propionamido]hexanoate	Amines and sulfhydryl	
hydrazide	Aldehydes, carbohydrates	
alkoxyamine	Aldehydes	
reductive amination	Amine	
aryl azide	Alkyne	

Diazirine, NHS diazirine, succinimidyl 4,4'-azipentanoate	Amine (through NHS group) to amine (UV 350 nm)	
azide-phosphine		
Aryl halide, 1,5-Difluoro-2,4-dinitrobenzene	Primary amines	

Chemical Structure
<chem>[N+](C)(C)CC(O)CC(=O)N[Low-MW silk-COOH]</chem>
<chem>[N+](C)(C)CC(O)CC(=O)N[Mid-MW silk-COOH]</chem>
<chem>NC(=O)CC(=O)N[Low-MW silk-COOH]</chem> <chem>NC(=O)CC(=O)N[Low-MW silk-COOH]</chem> <chem>NC(=O)CC(=O)N[Low-MW silk-COOH]</chem>
<chem>CCCC(=O)N[Mid-MW silk-COOH]</chem>

Structure
<chem>CC(=O)OC(O)CN[Low-MW silk-COOH]</chem>
<chem>CC(=O)N[Low-MW silk-COOH]</chem>
<chem>OC(=O)CC(=O)N[Low-MW silk-COOH]</chem>
<chem>CC(=O)NCCNC(=O)CC(=O)N[Low-MW silk-COOH]</chem>
<chem>CCCC(=O)N[Mid-MW silk-COOH]</chem>





Precursor linkers can be selected from any of the following natural crosslinkers: caffeic acid, tannic acid, genipin, proanthocyanidin, and the like. Precursor crosslinking can be selected from any of the following enzymatic crosslinking: transglutaminase transferase crosslinking, hydrolase crosslinking, peptidase crosslinking (e.g., sortase SrtA from *Staphylococcus aureus*), oxidoreductase crosslinking, tyrosinase crosslinking, laccase crosslinking, peroxidase crosslinking (e.g., horseradish peroxidase), lysyl oxidase crosslinking, peptide ligases (e.g., butelase 1, peptiligase, subtiligase, etc.), and the like.

In some embodiments, silk fibroin or silk fibroin-based protein fragments are chemically modified with a precursor linker to form silk conjugates with a crosslinker or an activator independently selected from a N-hydroxysuccinimide ester crosslinker, an imidoester crosslinker, a sulfosuccinimidyl aminobenzoate, a methacrylate, a silane, a silicate, an alkyne compound, an azide compound, an aldehyde, a carbodiimide crosslinker, a dicyclohexyl carbodiimide activator, a dicyclohexyl carbodiimide crosslinker, a maleimide crosslinker, a haloacetyl crosslinker, a pyridyl disulfide crosslinker, a hydrazide crosslinker, an alkoxyamine crosslinker, a reductive amination crosslinker, an aryl azide crosslinker, a diazirine crosslinker, an azide-phosphine crosslinker, a transferase crosslinker, a hydrolase crosslinker, a transglutaminase crosslinker, a peptidase crosslinker, an oxidoreductase crosslinker, a tyrosinase crosslinker, a laccase crosslinker, a peroxidase crosslinker, a lysyl oxidase crosslinker,

and any combinations thereof. Some chemically modified silk fibroin has been described in *J Mater Chem.* 2009, June 23, 19(36), 6443–6450, including cyanuric chloride-activated coupling, carbodiimide coupling, arginine masking, chlorosulfonic acid reaction, diazonium coupling, tyrosinase-catalyzed grafting, and poly(methacrylate) grafting.

Compositions and Processes Including Silk Fibroin-Based Coatings

In an embodiment, the disclosure may include textiles, such as fibers, yarns, fabrics, or other materials and combinations thereof, that may be coated with an SPF mixture solution (i.e., silk fibroin solution (SFS)) as described herein to produce a coated article, wherein the silk fibroin is chemically modified with a precursor linker to form a silk-conjugate, and wherein in some embodiments the silk fibroin is chemically linked to a substrate through the linker. In an embodiment, the coated articles described herein may be treated with additional chemical agents that may enhance the properties of the coated article. In an embodiment, the SFS may include one or more chemical agents that may enhance the properties of the coated article.

In an embodiment, textiles may be flexible materials (woven or non-woven) that include a network of natural and/or man-made fibers, thread, yarn, or a combination thereof. SFS may be applied at any stage of textile processing from individual fibers, to yarn, to fabric, to thread, or a combination thereof.

In an embodiment, fibers may be natural fibers that may include a natural fiber cellulose base, wherein the natural fiber cellulose base may include one or more of: (1) a bast such as flax, hemp, kenaf, jute, linen, and/or ramie; (2) a leaf such as flax, hemp, sisal, abaca, banana, henequen, ramie, sunn, and/or coir; and (3) seed hair such as cotton and/or kapok. In an embodiment, fibers may be natural fibers that may include a natural fiber protein base, wherein the natural fiber protein base may include one or more of: (1) hair such as alpaca, camel, cashmere, llama, mohair, and/or vicuna; (2) wool such as sheep; (3) filament such as silk. In an embodiment, fibers may be natural fibers that may include a natural fiber mineral base, including asbestos. In an embodiment, fibers may be man-made fibers that may include a man-made fiber organic natural polymer base, which may include one or more of: (1) a cellulose base such as bamboo, rayon, lyocell, acetate, and/or triacetate; (2) a protein base such as azlon; (3) an alginate; and (4) rubber. In an

embodiment, fibers may be man-made fibers that may include a man-made fiber organic synthetic base, which may include one or more of acrylic, anidex, aramid, fluorocarbon, modacrylic, novoloid, nylon, recycled nylon, nitril, olefin, PBI, polycarbonate, polyester, recycled polyester, rubber, saran, spandex, vinal vinon. In an embodiment, fibers may be man-made fibers that may include a man-made fiber inorganic base, which may include one or more of a glass material, metallic material, and carbon material.

In an embodiment, yarn may include natural fibers that may include a natural fiber cellulose base, wherein the natural fiber cellulose base may be from: (1) a bast such as flax, hemp, kenaf, jute, linen, and/or ramie; (2) a leaf such as flax, hemp, sisal, abaca, banana, henequen, ramie, sunn, and/or coir; or (3) seed hair such as cotton and/or kapok. In an embodiment, yarn may include natural fibers that may include a natural fiber protein base, wherein the natural fiber protein base may be from: (1) hair such as alpaca, camel, cashmere, llama, mohair, and/or vicuna; (2) wool such as sheep; or (3) filament such as silk. In an embodiment, yarn may include natural fibers that may include a natural fiber mineral base, including asbestos. In an embodiment, yarn may include man-made fibers that may include a man-made fiber organic natural polymer base, which may include: (1) a cellulose base such as bamboo, rayon, lyocell, acetate, and/or triacetate; (2) a protein base such as azlon; (3) an alginate; or (4) rubber. In an embodiment, yarn may include man-made fibers that may include a man-made fiber organic synthetic base, which may include acrylic, anidex, aramid, fluorocarbon, modacrylic, novoloid, nylon, recycled nylon, nitril, olefin, PBI, polycarbonate, polyester, recycled polyester, rubber, saran, spandex, vinal and/or vinon. In an embodiment, yarn may include man-made fibers that may include a man-made fiber inorganic base, which may include a glass material, metallic material, carbon material, and/or specialty material.

In an embodiment, fabrics may include natural fibers and/or yarn that may include a natural fiber cellulose base, wherein the natural fiber cellulose base may be from: (1) a bast such as flax, hemp, kenaf, jute, linen, and/or ramie; (2) a leaf such as flax, hemp, sisal, abaca, banana, henequen, ramie, sunn, and/or coir; or (3) seed hair such as cotton and/or kapok. In an embodiment, fabric may include natural fibers and/or yarn that may include a natural fiber protein base, wherein the natural fiber protein base may be from: (1) hair such as alpaca, camel, cashmere, llama, mohair, and/or vicuna; (2) wool such as

sheep; or (3) filament such as silk. In an embodiment, fabric may include natural fibers and/or yarn that may include a natural fiber mineral base, including asbestos. In an embodiment, fabric may include man-made fibers and/or yarn that may include a man-made fiber organic natural polymer base, which may include: (1) a cellulose base such as bamboo, rayon, lyocell, acetate, and/or triacetate; (2) a protein base such as azlon; (3) an alginate; or (4) rubber. In an embodiment, fabric may include man-made fibers and/or yarn that may include a man-made fiber organic synthetic base, which may include acrylic, anidex, aramid, fluorocarbon, modacrylic, novoloid, nylon, recycled nylon, nitril, olefin, PBI, polycarbonate, polyester, recycled polyester, rubber, saran, spandex, vinal and/or vinvon. In an embodiment, fabric may include man-made fibers and/or yarn that may include a man-made fiber inorganic base, which may include a glass material, metallic material, carbon material, and/or specialty material.

In an embodiment, textiles may be manufactured via one or more of the following processes weaving processes, knitting processes, and non-woven processes. In an embodiment, weaving processes may include plain weaving, twill weaving, and/or satin weaving. In an embodiment, knitting processes may include weft knitting (e.g., circular, flat bed, and/or full fashioned) and/or warp knitting (e.g., tricot, Raschel, and/or crochet). In an embodiment, non-woven processes may include staple fiber (e.g., dry laid and/or wet laid) and/or continuous filament (e.g., spun laid and/or melt blown).

In some embodiments, silk fibroin fragments may be applied to fibers and/or yarn having a diameter of less than about 100 nm, or less than about 200 nm, or less than about 300 nm, or less than about 400 nm, or less than about 500 nm, or less than about 600 nm, or less than about 700 nm, or less than about 800 nm, or less than about 900 nm, or less than about 1000 nm, or less than about 2 μm , or less than about 5 μm , or less than about 10 μm , or less than about 20 μm , or less than about 30 μm , or less than about 40 μm , or less than about 50 μm , or less than about 60 μm , or less than about 70 μm , or less than about 80 μm , or less than about 90 μm , or less than about 100 μm , or less than about 200 μm , or less than about 300 μm , or less than about 400 μm , or less than about 500 μm , or less than about 600 μm , or less than about 700 μm , or less than about 800 μm , or less than about 900 μm , or less than about 1000 μm , or less than about 2 mm, or less than about 3 mm, or less than about 4 mm, or less than about 5 mm, 6 mm, or less than about

7 mm, or less than about 8 mm, or less than about 9 mm, or less than about 10 mm, or less than about 20 mm, or less than about 30 mm, or less than about 40 mm, or less than about 50 mm, or less than about 60 mm, or less than about 70 mm, or less than about 80 mm, or less than about 90 mm, or less than about 100 mm, or less than about 200 mm, or less than about 300 mm, or less than about 400 mm, or less than about 500 mm, or less than about 600 mm, or less than about 700 mm, or less than about 800 mm, or less than about 900 mm, or less than about 1000 mm.

In some embodiments, silk fibroin fragments may be applied to fibers and/or yarn having a diameter of greater than about 100 nm, or greater than about 200 nm, or greater than about 300 nm, or greater than about 400 nm, or greater than about 500 nm, or greater than about 600 nm, or greater than about 700 nm, or greater than about 800 nm, or greater than about 900 nm, or greater than about 1000 nm, or greater than about 2 μm , or greater than about 5 μm , or greater than about 10 μm , or greater than about 20 μm , or greater than about 30 μm , or greater than about 40 μm , or greater than about 50 μm , or greater than about 60 μm , or greater than about 70 μm , or greater than about 80 μm , or greater than about 90 μm , or greater than about 100 μm , or greater than about 200 μm , or greater than about 300 μm , or greater than about 400 μm , or greater than about 500 μm , or greater than about 600 μm , or greater than about 700 μm , or greater than about 800 μm , or greater than about 900 μm , or greater than about 1000 μm , or greater than about 2 mm, or greater than about 3 mm, or greater than about 4 mm, or greater than about 5 mm, 6 mm, or greater than about 7 mm, or greater than about 8 mm, or greater than about 9 mm, or greater than about 10 mm, or greater than about 20 mm, or greater than about 30 mm, or greater than about 40 mm, or greater than about 50 mm, or greater than about 60 mm, or greater than about 70 mm, or greater than about 80 mm, or greater than about 90 mm, or greater than about 100 mm, or greater than about 200 mm, or greater than about 300 mm, or greater than about 400 mm, or greater than about 500 mm, or greater than about 600 mm, or greater than about 700 mm, or greater than about 800 mm, or greater than about 900 mm, or greater than about 1000 mm.

In some embodiments, silk fibroin fragments may be applied to fibers and/or yarn having a length of less than about 100 nm, or less than about 200 nm, or less than about 300 nm, or less than about 400 nm, or less than about 500 nm, or less than about 600 nm,

or less than about 700 nm, or less than about 800 nm, or less than about 900 nm, or less than about 1000 nm, or less than about 2 μm , or less than about 5 μm , or less than about 10 μm , or less than about 20 μm , or less than about 30 μm , or less than about 40 μm , or less than about 50 μm , or less than about 60 μm , or less than about 70 μm , or less than about 80 μm , or less than about 90 μm , or less than about 100 μm , or less than about 200 μm , or less than about 300 μm , or less than about 400 μm , or less than about 500 μm , or less than about 600 μm , or less than about 700 μm , or less than about 800 μm , or less than about 900 μm , or less than about 1000 μm , or less than about 2 mm, or less than about 3 mm, or less than about 4 mm, or less than about 5 mm, 6 mm, or less than about 7 mm, or less than about 8 mm, or less than about 9 mm, or less than about 10 mm, or less than about 20 mm, or less than about 30 mm, or less than about 40 mm, or less than about 50 mm, or less than about 60 mm, or less than about 70 mm, or less than about 80 mm, or less than about 90 mm, or less than about 100 mm, or less than about 200 mm, or less than about 300 mm, or less than about 400 mm, or less than about 500 mm, or less than about 600 mm, or less than about 700 mm, or less than about 800 mm, or less than about 900 mm, or less than about 1000 mm.

In some embodiments, silk fibroin fragments may be applied to fibers and/or yarn having a length of greater than about 100 nm, or greater than about 200 nm, or greater than about 300 nm, or greater than about 400 nm, or greater than about 500 nm, or greater than about 600 nm, or greater than about 700 nm, or greater than about 800 nm, or greater than about 900 nm, or greater than about 1000 nm, or greater than about 2 μm , or greater than about 5 μm , or greater than about 10 μm , or greater than about 20 μm , or greater than about 30 μm , or greater than about 40 μm , or greater than about 50 μm , or greater than about 60 μm , or greater than about 70 μm , or greater than about 80 μm , or greater than about 90 μm , or greater than about 100 μm , or greater than about 200 μm , or greater than about 300 μm , or greater than about 400 μm , or greater than about 500 μm , or greater than about 600 μm , or greater than about 700 μm , or greater than about 800 μm , or greater than about 900 μm , or greater than about 1000 μm , or greater than about 2 mm, or greater than about 3 mm, or greater than about 4 mm, or greater than about 5 mm, 6 mm, or greater than about 7 mm, or greater than about 8 mm, or greater than about 9 mm, or greater than about 10 mm, or greater than about 20 mm, or greater than about 30 mm,

or greater than about 40 mm, or greater than about 50 mm, or greater than about 60 mm, or greater than about 70 mm, or greater than about 80 mm, or greater than about 90 mm, or greater than about 100 mm, or greater than about 200 mm, or greater than about 300 mm, or greater than about 400 mm, or greater than about 500 mm, or greater than about 600 mm, or greater than about 700 mm, or greater than about 800 mm, or greater than about 900 mm, or greater than about 1000 mm.

In some embodiments, silk fibroin fragments may be applied to fibers and/or yarn having a weight (g/m^2) of less than about 1 g/m^2 , or less than about 2 g/m^2 , or less than about 3 g/m^2 , or less than about 4 g/m^2 , or less than about 5 g/m^2 , or less than about 6 g/m^2 , or less than about 7 g/m^2 , or less than about 8 g/m^2 , or less than about 9 g/m^2 , or less than about 10 g/m^2 , or less than about 20 g/m^2 , or less than about 30 g/m^2 , or less than about 40 g/m^2 , or less than about 50 g/m^2 , or less than about 60 g/m^2 , or less than about 70 g/m^2 , or less than about 80 g/m^2 , or less than about 90 g/m^2 , or less than about 100 g/m^2 , or less than about 200 g/m^2 , or less than about 300 g/m^2 , or less than about 400 g/m^2 , or less than about 500 g/m^2 .

In some embodiments, silk fibroin fragments may be applied to fibers and/or yarn having a weight (g/m^2) of at greater than about 1 g/m^2 , or greater than about 2 g/m^2 , or greater than about 3 g/m^2 , or greater than about 4 g/m^2 , or greater than about 5 g/m^2 , or greater than about 6 g/m^2 , or greater than about 7 g/m^2 , or greater than about 8 g/m^2 , or greater than about 9 g/m^2 , or greater than about 10 g/m^2 , or greater than about 20 g/m^2 , or greater than about 30 g/m^2 , or greater than about 40 g/m^2 , or greater than about 50 g/m^2 , or greater than about 60 g/m^2 , or greater than about 70 g/m^2 , or greater than about 80 g/m^2 , or greater than about 90 g/m^2 , or greater than about 100 g/m^2 , or greater than about 200 g/m^2 , or greater than about 300 g/m^2 , or greater than about 400 g/m^2 , or greater than about 500 g/m^2 .

In some embodiments, silk fibroin fragments may be applied to fabric having a thickness of less than about 100 nm, or less than about 200 nm, or less than about 300 nm, or less than about 400 nm, or less than about 500 nm, or less than about 600 nm, or less than about 700 nm, or less than about 800 nm, or less than about 900 nm, or less than about 1000 nm, or less than about 2 μm , or less than about 5 μm , or less than about 10 μm , or less than about 20 μm , or less than about 30 μm , or less than about 40 μm , or less

than about 50 μm , or less than about 60 μm , or less than about 70 μm , or less than about 80 μm , or less than about 90 μm , or less than about 100 μm , or less than about 200 μm , or less than about 300 μm , or less than about 400 μm , or less than about 500 μm , or less than about 600 μm , or less than about 700 μm , or less than about 800 μm , or less than about 900 μm , or less than about 1000 μm , or less than about 2 mm, or less than about 3 mm, or less than about 4 mm, or less than about 5 mm, 6 mm, or less than about 7 mm, or less than about 8 mm, or less than about 9 mm, or less than about 10 mm.

In some embodiments, silk fibroin fragments may be applied to fabric having a thickness of greater than about 100 nm, or greater than about 200 nm, or greater than about 300 nm, or greater than about 400 nm, or greater than about 500 nm, or greater than about 600 nm, or greater than about 700 nm, or greater than about 800 nm, or greater than about 900 nm, or greater than about 1000 nm, or greater than about 2 μm , or greater than about 5 μm , or greater than about 10 μm , or greater than about 20 μm , or greater than about 30 μm , or greater than about 40 μm , or greater than about 50 μm , or greater than about 60 μm , or greater than about 70 μm , or greater than about 80 μm , or greater than about 90 μm , or greater than about 100 μm , or greater than about 200 μm , or greater than about 300 μm , or greater than about 400 μm , or greater than about 500 μm , or greater than about 600 μm , or greater than about 700 μm , or greater than about 800 μm , or greater than about 900 μm , or greater than about 1000 μm , or greater than about 2 mm, or greater than about 3 mm, or greater than about 4 mm, or greater than about 5 mm, 6 mm, or greater than about 7 mm, or greater than about 8 mm, or greater than about 9 mm, or greater than about 10 mm.

In some embodiments, silk fibroin fragments may be applied to fabric having a width of less than about 100 nm, or less than about 200 nm, or less than about 300 nm, or less than about 400 nm, or less than about 500 nm, or less than about 600 nm, or less than about 700 nm, or less than about 800 nm, or less than about 900 nm, or less than about 1000 nm, or less than about 2 μm , or less than about 5 μm , or less than about 10 μm , or less than about 20 μm , or less than about 30 μm , or less than about 40 μm , or less than about 50 μm , or less than about 60 μm , or less than about 70 μm , or less than about 80 μm , or less than about 90 μm , or less than about 100 μm , or less than about 200 μm , or less than about 300 μm , or less than about 400 μm , or less than about 500 μm , or less

than about 600 μm , or less than about 700 μm , or less than about 800 μm , or less than about 900 μm , or less than about 1000 μm , or less than about 2 mm, or less than about 3 mm, or less than about 4 mm, or less than about 5 mm, 6 mm, or less than about 7 mm, or less than about 8 mm, or less than about 9 mm, or less than about 10 mm, or less than about 20 mm, or less than about 30 mm, or less than about 40 mm, or less than about 50 mm, or less than about 60 mm, or less than about 70 mm, or less than about 80 mm, or less than about 90 mm, or less than about 100 mm, or less than about 200 mm, or less than about 300 mm, or less than about 400 mm, or less than about 500 mm, or less than about 600 mm, or less than about 700 mm, or less than about 800 mm, or less than about 900 mm, or less than about 1000 mm, or less than about 2 m, or less than about 3 m, or less than about 4 m, or less than about 5 m.

In some embodiments, silk fibroin fragments may be applied to fabric having a width of greater than about 100 nm, or greater than about 200 nm, or greater than about 300 nm, or greater than about 400 nm, or greater than about 500 nm, or greater than about 600 nm, or greater than about 700 nm, or greater than about 800 nm, or greater than about 900 nm, or greater than about 1000 nm, or greater than about 2 μm , or greater than about 5 μm , or greater than about 10 μm , or greater than about 20 μm , or greater than about 30 μm , or greater than about 40 μm , or greater than about 50 μm , or greater than about 60 μm , or greater than about 70 μm , or greater than about 80 μm , or greater than about 90 μm , or greater than about 100 μm , or greater than about 200 μm , or greater than about 300 μm , or greater than about 400 μm , or greater than about 500 μm , or greater than about 600 μm , or greater than about 700 μm , or greater than about 800 μm , or greater than about 900 μm , or greater than about 1000 μm , or greater than about 2 mm, or greater than about 3 mm, or greater than about 4 mm, or greater than about 5 mm, 6 mm, or greater than about 7 mm, or greater than about 8 mm, or greater than about 9 mm, or greater than about 10 mm, or greater than about 20 mm, or greater than about 30 mm, or greater than about 40 mm, or greater than about 50 mm, or greater than about 60 mm, or greater than about 70 mm, or greater than about 80 mm, or greater than about 90 mm, or greater than about 100 mm, or greater than about 200 mm, or greater than about 300 mm, or greater than about 400 mm, or greater than about 500 mm, or greater than about 600 mm, or greater than about 700 mm, or greater than about 800 mm, or greater than about

900 mm, or greater than about 1000 mm, or greater than about 2 m, or greater than about 3 m, or greater than about 4 m, or greater than about 5 m.

In some embodiments, silk fibroin fragments may be applied to fabric having a length of less than about 100 nm, or less than about 200 nm, or less than about 300 nm, or less than about 400 nm, or less than about 500 nm, or less than about 600 nm, or less than about 700 nm, or less than about 800 nm, or less than about 900 nm, or less than about 1000 nm, or less than about 2 μm , or less than about 5 μm , or less than about 10 μm , or less than about 20 μm , or less than about 30 μm , or less than about 40 μm , or less than about 50 μm , or less than about 60 μm , or less than about 70 μm , or less than about 80 μm , or less than about 90 μm , or less than about 100 μm , or less than about 200 μm , or less than about 300 μm , or less than about 400 μm , or less than about 500 μm , or less than about 600 μm , or less than about 700 μm , or less than about 800 μm , or less than about 900 μm , or less than about 1000 μm , or less than about 2 mm, or less than about 3 mm, or less than about 4 mm, or less than about 5 mm, 6 mm, or less than about 7 mm, or less than about 8 mm, or less than about 9 mm, or less than about 10 mm, or less than about 20 mm, or less than about 30 mm, or less than about 40 mm, or less than about 50 mm, or less than about 60 mm, or less than about 70 mm, or less than about 80 mm, or less than about 90 mm, or less than about 100 mm, or less than about 200 mm, or less than about 300 mm, or less than about 400 mm, or less than about 500 mm, or less than about 600 mm, or less than about 700 mm, or less than about 800 mm, or less than about 900 mm, or less than about 1000 mm.

In some embodiments, silk fibroin fragments may be applied to fabric having a length of greater than about 100 nm, or greater than about 200 nm, or greater than about 300 nm, or greater than about 400 nm, or greater than about 500 nm, or greater than about 600 nm, or greater than about 700 nm, or greater than about 800 nm, or greater than about 900 nm, or greater than about 1000 nm, or greater than about 2 μm , or greater than about 5 μm , or greater than about 10 μm , or greater than about 20 μm , or greater than about 30 μm , or greater than about 40 μm , or greater than about 50 μm , or greater than about 60 μm , or greater than about 70 μm , or greater than about 80 μm , or greater than about 90 μm , or greater than about 100 μm , or greater than about 200 μm , or greater than about 300 μm , or greater than about 400 μm , or greater than about 500 μm , or greater than

about 600 μm , or greater than about 700 μm , or greater than about 800 μm , or greater than about 900 μm , or greater than about 1000 μm , or greater than about 2 mm, or greater than about 3 mm, or greater than about 4 mm, or greater than about 5 mm, 6 mm, or greater than about 7 mm, or greater than about 8 mm, or greater than about 9 mm, or greater than about 10 mm, or greater than about 20 mm, or greater than about 30 mm, or greater than about 40 mm, or greater than about 50 mm, or greater than about 60 mm, or greater than about 70 mm, or greater than about 80 mm, or greater than about 90 mm, or greater than about 100 mm, or greater than about 200 mm, or greater than about 300 mm, or greater than about 400 mm, or greater than about 500 mm, or greater than about 600 mm, or greater than about 700 mm, or greater than about 800 mm, or greater than about 900 mm, or greater than about 1000 mm.

In some embodiments, silk fibroin fragments may be applied to fabric having a stretch percentage of less than about 1 %, or less than about 2 %, or less than about 3 %, or less than about 4 %, or less than about 5 %, or less than about 6 %, or less than about 7 %, or less than about 8 %, or less than about 9 %, or less than about 10 %, or less than about 20 %, or less than about 30 %, or less than about 40 %, or less than about 50 %, or less than about 60 %, or less than about 70 %, or less than about 80 %, or less than about 90 %, or less than about 100 %, or less than about 110 %, or less than about 120 %, or less than about 130 %, or less than about 140 %, or less than about 150 %, or less than about 160 %, or less than about 170 %, or less than about 180 %, or less than about 190 %, or less than about 200 %. Stretch percentage may be determined for a fabric having an unstretched width and stretching the fabric to a stretched width, then subtracting the unstretched width from the stretched width to yield the net stretched width, then dividing the net stretched width and multiplying the quotient by 100 to find the stretch percentage (%):

$$\text{Stretch Percentage} = \frac{(\text{Stretched Width} - \text{Unstretched Width})}{\text{Unstretched Width}} * 100$$

In some embodiments, silk fibroin fragments may be applied to fabric having a stretch percentage of greater than about 1 %, or greater than about 2 %, or greater than about 3 %, or greater than about 4 %, or greater than about 5 %, or greater than about 6 %, or greater than about 7 %, or greater than about 8 %, or greater than about 9 %, or

greater than about 10 %, or greater than about 20 %, or greater than about 30 %, or greater than about 40 %, or greater than about 50 %, or greater than about 60 %, or greater than about 70 %, or greater than about 80 %, or greater than about 90 %, or greater than about 100 %, or greater than about 110 %, or greater than about 120 %, or greater than about 130 %, or greater than about 140 %, or greater than about 150 %, or greater than about 160 %, or greater than about 170 %, or greater than about 180 %, or greater than about 190 %, or greater than about 200 %

In some embodiments, silk fibroin fragments may be applied to fabric having a tensile energy (N/cm²) of less than about 1 cN/cm², or less than about 2 cN/cm², or less than about 3 cN/cm², or less than about 4 cN/cm², or less than about 5 cN/cm², or less than about 6 cN/cm², or less than about 7 cN/cm², or less than about 8 cN/cm², or less than about 9 cN/cm², or less than about 10 cN/cm², or less than about 20 cN/cm², or less than about 30 cN/cm², or less than about 40 cN/cm², or less than about 50 cN/cm², or less than about 60 cN/cm², or less than about 70 cN/cm², or less than about 80 cN/cm², or less than about 90 cN/cm², or less than about 100 cN/cm², or less than about 2 N/cm², or less than about 3 N/cm², or less than about 4 N/cm², or less than about 5 N/cm², or less than about 6 N/cm², or less than about 7 N/cm², or less than about 8 N/cm², or less than about 9 N/cm², or less than about 10 N/cm², or less than about 20 N/cm², or less than about 30 N/cm², or less than about 40 N/cm², or less than about 50 N/cm², or less than about 60 N/cm², or less than about 70 N/cm², or less than about 80 N/cm², or less than about 90 N/cm², or less than about 100 N/cm², or less than about 150 N/cm², or less than about 200 N/cm².

In some embodiments, silk fibroin fragments may be applied to fabric having a tensile energy (N/cm²) of greater than about 1 cN/cm², or greater than about 2 cN/cm², or greater than about 3 cN/cm², or greater than about 4 cN/cm², or greater than about 5 cN/cm², or greater than about 6 cN/cm², or greater than about 7 cN/cm², or greater than about 8 cN/cm², or greater than about 9 cN/cm², or greater than about 10 cN/cm², or greater than about 20 cN/cm², or greater than about 30 cN/cm², or greater than about 40 cN/cm², or greater than about 50 cN/cm², or greater than about 60 cN/cm², or greater than about 70 cN/cm², or greater than about 80 cN/cm², or greater than about 90 cN/cm², or greater than about 100 cN/cm², or greater than about 2

N/cm², or greater than about 3 N/cm², or greater than about 4 N/cm², or greater than about 5 N/cm², or greater than about 6 N/cm², or greater than about 7 N/cm², or greater than about 8 N/cm², or greater than about 9 N/cm², or greater than about 10 N/cm², or greater than about 20 N/cm², or greater than about 30 N/cm², or greater than about 40 N/cm², or greater than about 50 N/cm², or greater than about 60 N/cm², or greater than about 70 N/cm², or greater than about 80 N/cm², or greater than about 90 N/cm², or greater than about 100 N/cm², or greater than about 150 N/cm², or greater than about 200 N/cm².

In some embodiments, silk fibroin fragments may be applied to fabric having a shear rigidity (N/cm-degree) of less than about 1 cN/cm-degree, or less than about 2 cN/cm-degree, or less than about 3 cN/cm-degree, or less than about 4 cN/cm-degree, or less than about 5 cN/cm-degree, or less than about 5 cN/cm-degree, or less than about 6 cN/cm-degree, or less than about 7 cN/cm-degree, or less than about 8 cN/cm-degree, or less than about 9 cN/cm-degree, or less than about 10 cN/cm-degree, or less than about 20 cN/cm-degree, or less than about 30 cN/cm-degree, or less than about 40 cN/cm-degree, or less than about 50 cN/cm-degree, or less than about 60 cN/cm-degree, or less than about 70 cN/cm-degree, or less than about 80 cN/cm-degree, or less than about 90 cN/cm-degree, or less than about 100 cN/cm-degree, or less than about 2 N/cm-degree, or less than about 3 N/cm-degree, or less than about 4 N/cm-degree, or less than about 5 N/cm-degree, or less than about 6 N/cm-degree, or less than about 7 N/cm-degree, or less than about 8 N/cm-degree, or less than about 9 N/cm-degree, or less than about 10 N/cm-degree, or less than about 20 N/cm-degree, or less than about 30 N/cm-degree, or less than about 40 N/cm-degree, or less than about 50 N/cm-degree, or less than about 60 N/cm-degree, or less than about 70 N/cm-degree, or less than about 80 N/cm-degree, or less than about 90 N/cm-degree, or less than about 100 N/cm-degree, or less than about 150 N/cm-degree, or less than about 200 N/cm-degree.

In some embodiments, silk fibroin fragments may be applied to fabric having a shear rigidity (N/cm-degree) of greater than about 1 cN/cm-degree, or greater than about 2 cN/cm-degree, or greater than about 3 cN/cm-degree, or greater than about 4 cN/cm-degree, or greater than about 5 cN/cm-degree, or greater than about 5 cN/cm-degree, or greater than about 6 cN/cm-degree, or greater than about 7 cN/cm-degree, or greater than

about 8 cN/cm-degree, or greater than about 9 cN/cm-degree, or greater than about 10 cN/cm-degree, or greater than about 20 cN/cm-degree, or greater than about 30 cN/cm-degree, or greater than about 40 cN/cm-degree, or greater than about 50 cN/cm-degree, or greater than about 60 cN/cm-degree, or greater than about 70 cN/cm-degree, or greater than about 80 cN/cm-degree, or greater than about 90 cN/cm-degree, or greater than about 100 cN/cm-degree, or greater than about 2 N/cm-degree, or greater than about 3 N/cm-degree, or greater than about 4 N/cm-degree, or greater than about 5 N/cm-degree, or greater than about 6 N/cm-degree, or greater than about 7 N/cm-degree, or greater than about 8 N/cm-degree, or greater than about 9 N/cm-degree, or greater than about 10 N/cm-degree, or greater than about 20 N/cm-degree, or greater than about 30 N/cm-degree, or greater than about 40 N/cm-degree, or greater than about 50 N/cm-degree, or greater than about 60 N/cm-degree, or greater than about 70 N/cm-degree, or greater than about 80 N/cm-degree, or greater than about 90 N/cm-degree, or greater than about 100 N/cm-degree, or greater than about 150 N/cm-degree, or greater than about 200 N/cm-degree.

In some embodiments, silk fibroin fragments may be applied to fabric having a bending rigidity ($\text{N}\cdot\text{cm}^2/\text{cm}$) of less than about 1 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 2 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 3 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 4 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 5 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 6 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 7 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 8 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 9 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 10 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 20 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 30 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 40 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 50 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 60 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 70 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 80 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 90 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 100 $\text{cN}\cdot\text{cm}^2/\text{cm}$, or less than about 2 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 3 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 4 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 5 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 6 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 7 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 8 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 9 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 10 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 20 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 30 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 40 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 50 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 60 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 70 $\text{N}\cdot\text{cm}^2/\text{cm}$, or less than about 80 $\text{N}\cdot\text{cm}^2/\text{cm}$, or

less than about 90 N•cm²/cm, or less than about 100 N•cm²/cm, or less than about 150 N•cm²/cm, or less than about 200 N•cm²/cm.

In some embodiments, silk fibroin fragments may be applied to fabric having a bending rigidity (N•cm²/cm) of greater than about 1 cN•cm²/cm, or greater than about 2 cN•cm²/cm, or greater than about 3 cN•cm²/cm, or greater than about 4 cN•cm²/cm, or greater than about 5 cN•cm²/cm, or greater than about 5 cN•cm²/cm, or greater than about 6 cN•cm²/cm, or greater than about 7 cN•cm²/cm, or greater than about 8 cN•cm²/cm, or greater than about 9 cN•cm²/cm, or greater than about 10 cN•cm²/cm, or greater than about 20 cN•cm²/cm, or greater than about 30 cN•cm²/cm, or greater than about 40 cN•cm²/cm, or greater than about 50 cN•cm²/cm, or greater than about 60 cN•cm²/cm, or greater than about 70 cN•cm²/cm, or greater than about 80 cN•cm²/cm, or greater than about 90 cN•cm²/cm, or greater than about 100 cN•cm²/cm, or greater than about 2 N•cm²/cm, or greater than about 3 N•cm²/cm, or greater than about 4 N•cm²/cm, or greater than about 5 N•cm²/cm, or greater than about 6 N•cm²/cm, or greater than about 7 N•cm²/cm, or greater than about 8 N•cm²/cm, or greater than about 9 N•cm²/cm, or greater than about 10 N•cm²/cm, or greater than about 20 N•cm²/cm, or greater than about 30 N•cm²/cm, or greater than about 40 N•cm²/cm, or greater than about 50 N•cm²/cm, or greater than about 60 N•cm²/cm, or greater than about 70 N•cm²/cm, or greater than about 80 N•cm²/cm, or greater than about 90 N•cm²/cm, or greater than about 100 N•cm²/cm, or greater than about 150 N•cm²/cm, or greater than about 200 N•cm²/cm.

In some embodiments, silk fibroin fragments may be applied to fabric having a compression energy (N•cm/cm²) of less than about 1 cN•cm/cm², or less than about 2 cN•cm/cm², or less than about 3 cN•cm/cm², or less than about 4 cN•cm/cm², or less than about 5 cN•cm/cm², or less than about 5 cN•cm/cm², or less than about 6 cN•cm/cm², or less than about 7 cN•cm/cm², or less than about 8 cN•cm/cm², or less than about 9 cN•cm/cm², or less than about 10 cN•cm/cm², or less than about 20 cN•cm/cm², or less than about 30 cN•cm/cm², or less than about 40 cN•cm/cm², or less than about 50 cN•cm/cm², or less than about 60 cN•cm/cm², or less than about 70 cN•cm/cm², or less than about 80 cN•cm/cm², or less than about 90 cN•cm/cm², or less than about 100 cN•cm/cm², or less than about 2 N•cm/cm², or less than about 3 N•cm/cm², or less than

about 4 N•cm/cm², or less than about 5 N•cm/cm², or less than about 6 N•cm/cm², or less than about 7 N•cm/cm², or less than about 8 N•cm/cm², or less than about 9 N•cm/cm², or less than about 10 N•cm/cm², or less than about 20 N•cm/cm², or less than about 30 N•cm/cm², or less than about 40 N•cm/cm², or less than about 50 N•cm/cm², or less than about 60 N•cm/cm², or less than about 70 N•cm/cm², or less than about 80 N•cm/cm², or less than about 90 N•cm/cm², or less than about 100 N•cm/cm², or less than about 150 N•cm/cm², or less than about 200 N•cm/cm².

In some embodiments, silk fibroin fragments may be applied to fabric having a compression energy (N•cm/cm²) of greater than about 1 cN•cm/cm², or greater than about 2 cN•cm/cm², or greater than about 3 cN•cm/cm², or greater than about 4 cN•cm/cm², or greater than about 5 cN•cm/cm², or greater than about 5 cN•cm/cm², or greater than about 6 cN•cm/cm², or greater than about 7 cN•cm/cm², or greater than about 8 cN•cm/cm², or greater than about 9 cN•cm/cm², or greater than about 10 cN•cm/cm², or greater than about 20 cN•cm/cm², or greater than about 30 cN•cm/cm², or greater than about 40 cN•cm/cm², or greater than about 50 cN•cm/cm², or greater than about 60 cN•cm/cm², or greater than about 70 cN•cm/cm², or greater than about 80 cN•cm/cm², or greater than about 90 cN•cm/cm², or greater than about 100 cN•cm/cm², or greater than about 2 N•cm/cm², or greater than about 3 N•cm/cm², or greater than about 4 N•cm/cm², or greater than about 5 N•cm/cm², or greater than about 6 N•cm/cm², or greater than about 7 N•cm/cm², or greater than about 8 N•cm/cm², or greater than about 9 N•cm/cm², or greater than about 10 N•cm/cm², or greater than about 20 N•cm/cm², or greater than about 30 N•cm/cm², or greater than about 40 N•cm/cm², or greater than about 50 N•cm/cm², or greater than about 60 N•cm/cm², or greater than about 70 N•cm/cm², or greater than about 80 N•cm/cm², or greater than about 90 N•cm/cm², or greater than about 100 N•cm/cm², or greater than about 150 N•cm/cm², or greater than about 200 N•cm/cm².

In some embodiments, silk fibroin fragments may be applied to fabric having a coefficient of friction of less than about 0.04, or less than about 0.05, or less than about 0.06, or less than about 0.07, or less than about 0.08, or less than about 0.09, or less than about 0.10, or less than about 0.10, or less than about 0.15, or less than about 0.20, or less than about 0.25, or less than about 0.30, or less than about 0.35, or less than about 0.40,

or less than about 0.45, or less than about 0.50, or less than about 0.55, or less than about 0.60, or less than about 0.65, or less than about 0.70, or less than about 0.75, or less than about 0.80, or less than about 0.85, or less than about 0.90, or less than about 0.95, or less than about 1.00, or less than about 1.05.

In some embodiments, silk fibroin fragments may be applied to fabric having a coefficient of friction of greater than about 0.04, or greater than about 0.05, or greater than about 0.06, or greater than about 0.07, or greater than about 0.08, or greater than about 0.09, or greater than about 0.10, or greater than about 0.10, or greater than about 0.15, or greater than about 0.20, or greater than about 0.25, or greater than about 0.30, or greater than about 0.35, or greater than about 0.40, or greater than about 0.45, or greater than about 0.50, or greater than about 0.55, or greater than about 0.60, or greater than about 0.65, or greater than about 0.70, or greater than about 0.75, or greater than about 0.80, or greater than about 0.85, or greater than about 0.90, or greater than about 0.95, or greater than about 1.00, or greater than about 1.05.

In some embodiments, chemical finishes may be applied to textiles before or after such textiles are coated with SFS. In an embodiment, chemical finishing may be intended as the application of chemical agents and/or SFS to textiles, including fibers, yarn, and fabric, or to garments that are prepared by such fibers, yarn, and fabric to modify the original textile's or garment's properties and achieve properties in the textile or garment that would be otherwise absent. With chemical finishes, textiles treated with such chemical finishes may act as surface treatments and/or the treatments may modify the elemental analysis of treated textile base polymers.

In an embodiment, a type of chemical finishing may include the application of certain silk-fibroin based solutions to textiles. For example, SFS may be applied to a fabric after it is dyed, but there are also scenarios that may require the application of SFS during processing, during dyeing, or after a garment is assembled from a selected textile or fabric, thread, or yarn. In some embodiments, after its application, SFS may be dried with the use of heat. SFS may then be fixed to the surface of the textile in a processing step called curing.

In some embodiments, silk fibroin fragments may be supplied in a concentrated form suspended in water. In some embodiments, silk fibroin fragments may have a

concentration by weight (% w/w or % w/v) or by volume (v/v) of less than about 50 %, or less than about 45%, or less than about 40%, or less than about 35%, or less than about 30%, or less than about 25%, or less than about 20%, or less than about 15%, or less than about 10%, or less than about 5%, or less than about 4%, or less than about 3%, or less than about 2%, or less than about 1%, or less than about 0.1%, or less than about 0.01%, or less than about 0.001%, or less than about 0.0001%, or less than about 0.00001%. In some embodiments, SFS may have a concentration by weight (% w/w or % w/v) or by volume (v/v) of greater than about 50 %, or greater than about 45%, or greater than about 40%, or greater than about 35%, or greater than about 30%, or greater than about 25%, or greater than about 20%, or greater than about 15%, or greater than about 10%, or greater than about 5%, or greater than about 4%, or greater than about 3%, or greater than about 2%, or greater than about 1%, or greater than about 0.1%, or greater than about 0.01%, or greater than about 0.001%, or greater than about 0.0001%, or greater than about 0.00001%.

In some embodiments, the solution concentration and the wet pick of the material determines the amount of silk fibroin solution, which may include silk-based proteins or fragments thereof, that may be fixed or otherwise adhered to the textile being coated. The wet pick up may be expressed by the following formula:

$$\text{wet pick up}(\%) = \frac{\text{weight of SFS applied} \times 100}{\text{weight of dry textile material}}.$$

The total amount of silk fibroin fragments added to the textile material may be expressed by the following formula:

$$\text{SFS added}(\%) = \frac{\text{weight of dry SFS coated textile material} \times 100}{\text{weight of dry textile material before coating}}.$$

Regarding methods for applying silk fibroin fragments to textiles more broadly, silk fibroin fragments may be applied to textiles by methods known in the art, for example methods described in U.S. Patent Application Publications Nos. 20160222579, 20160281294, and 20190003113.

In an embodiment, “substantially modifying” silk fibroin coating performance may be a decrease in a selected property of silk fibroin coating, such as wetting time, absorption rate, spreading speed, accumulative one-way transport, or overall moisture management capability as compared to a control silk fibroin coating that was not subjected to the selected temperature for drying, curing, wash cycling, and/or heat setting purposes, where such decrease is less than about a 1% decrease, or less than about a 2 % decrease, or less than about a 3 % decrease, or less than about a 4 % decrease, or less than about a 5 % decrease, or less than about a 6 % decrease, or less than about a 7 % decrease, or less than about an 8 % decrease, or less than about a 9 % decrease, or less than about a 10 % decrease, or less than about a 15 % decrease, or less than about a 20 % decrease, or less than about a 25 % decrease, or less than about a 30 % decrease, or less than about a 35 % decrease, or less than about a 40 % decrease, or less than about a 45 % decrease, or less than about a 50 % decrease, or less than about a 60% decrease, or less than about a 70 % decrease, or less than about a 80 % decrease, or less than about a 90 % decrease, or less than about 100 % decrease in wetting time, absorption rate, spreading speed, accumulative one-way transport, or overall moisture management capability as compared to a control silk fibroin coating that was not subjected to the selected temperature for drying, curing, wash cycling, and/or heat setting purposes. In some embodiments, “wash cycling” may refer to at least one wash cycle, or at least two wash cycles, or at least three wash cycles, or at least four wash cycles, or at least five wash cycles.

In an embodiment, “substantially modifying” silk fibroin coating performance may be an increase in a selected property of silk fibroin coating, such as wetting time, absorption rate, spreading speed, accumulative one-way transport, or overall moisture management capability as compared to a control silk fibroin coating that was not subjected to the selected temperature for drying, curing, wash cycling, and/or heat setting purposes, where such increase is less than about a 1% increase, or less than about a 2 % increase, or less than about a 3 % increase, or less than about a 4 % increase, or less than

about a 5 % increase, or less than about a 6 % increase, or less than about a 7 % increase, or less than about an 8 % increase, or less than about a 9 % increase, or less than about a 10 % increase, or less than about a 15 % increase, or less than about a 20 % increase, or less than about a 25 % increase, or less than about a 30 % increase, or less than about a 35 % increase, or less than about a 40 % increase, or less than about a 45 % increase, or less than about a 50 % increase, or less than about a 60% increase, or less than about a 70 % increase, or less than about a 80 % increase, or less than about a 90 % increase, or less than about 100 % increase in wetting time, absorption rate, spreading speed, accumulative one-way transport, or overall moisture management capability as compared to a control silk fibroin coating that was not subjected to the selected temperature for drying, curing, wash cycling, and/or heat setting purposes. In some embodiments, “wash cycling” may refer to at least one wash cycle, or at least two wash cycles, or at least three wash cycles, or at least four wash cycles, or at least five wash cycles.

In some embodiments, silk fibroin fragments may be used in combination with chemical agents. In some embodiments, silk fibroin fragments may be applied in conjunction with a chemical agent, for example a chemical modifier and/or a physical modifier. In some embodiments, the chemical modifier is chemically linked to one or more of a silk fibroin side group and a silk fibroin terminal group. In some embodiments, the silk fibroin side group and the silk fibroin terminal group are independently selected from an amine group, an amide group, a carboxyl group, a hydroxyl group, a thiol group, and a sulfhydryl group. In some embodiments, the chemical modifier is chemically linked to one or more functional groups on the substrate. In some embodiments, the functional group on the substrate is selected from an amine group, an amide group, a carboxyl group, a hydroxyl group, a thiol group, and a sulfhydryl group. In some embodiments, the chemical modifier includes one or more of a chemically linked functional group, or functional group residue, and a linker. In some embodiments, the chemical modifier includes one or more of $-\text{CR}^a_2-$, $-\text{CR}^a=\text{CR}^a-$, $-\text{C}\equiv\text{C}-$, $-\text{alkyl}-$, $-\text{alkenyl}-$, $-\text{alkynyl}-$, $-\text{aryl}-$, $-\text{heteroaryl}-$, $-\text{O}-$, $-\text{S}-$, $-\text{OC}(\text{O})-$, $-\text{N}(\text{R}^a)-$, $-\text{N}=\text{N}-$, $=\text{N}-$, $-\text{C}(\text{O})-$, $-\text{C}(\text{O})\text{O}-$, $-\text{OC}(\text{O})\text{N}(\text{R}^a)-$, $-\text{C}(\text{O})\text{N}(\text{R}^a)-$, $-\text{N}(\text{R}^a)\text{C}(\text{O})\text{O}-$, $-\text{N}(\text{R}^a)\text{C}(\text{O})-$, $-\text{N}(\text{R}^a)\text{C}(\text{O})\text{N}(\text{R}^a)-$, $-\text{N}(\text{R}^a)\text{C}(\text{NR}^a)\text{N}(\text{R}^a)-$, $-\text{N}(\text{R}^a)\text{S}(\text{O})_t-$, $-\text{S}(\text{O})_t\text{O}-$, $-\text{S}(\text{O})_t\text{N}(\text{R}^a)-$, $-\text{S}(\text{O})_t\text{N}(\text{R}^a)\text{C}(\text{O})-$, $-\text{OP}(\text{O})(\text{OR}^a)\text{O}-$, wherein t is 1 or 2, and wherein at each independent occurrence R^a is selected from hydrogen, alkyl,

alkenyl, fluoroalkyl, carbocyclyl, carbocyclylalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl, or heteroarylalkyl.

“Alkyl” refers to a straight or branched hydrocarbon chain radical consisting solely of carbon and hydrogen atoms, containing no unsaturation, having from one to ten carbon atoms (*e.g.*, (C₁₋₁₀)alkyl or C₁₋₁₀ alkyl). Whenever it appears herein, a numerical range such as “1 to 10” refers to each integer in the given range - *e.g.*, “1 to 10 carbon atoms” means that the alkyl group may consist of 1 carbon atom, 2 carbon atoms, 3 carbon atoms, *etc.*, up to and including 10 carbon atoms, although the definition is also intended to cover the occurrence of the term “alkyl” where no numerical range is specifically designated. Typical alkyl groups include, but are in no way limited to, methyl, ethyl, propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, isobutyl, tertiary butyl, pentyl, isopentyl, neopentyl, hexyl, heptyl, octyl, nonyl and decyl. The alkyl moiety may be attached to the rest of the molecule by a single bond, such as for example, methyl (Me), ethyl (Et), *n*-propyl (Pr), 1-methylethyl (isopropyl), *n*-butyl, *n*-pentyl, 1,1-dimethylethyl (*t*-butyl) and 3-methylhexyl. Unless stated otherwise specifically in the specification, an alkyl group is optionally substituted by one or more of substituents which are independently heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, -OR^a, -SR^a, -OC(O)-R^a, -N(R^a)₂, -C(O)R^a, -C(O)OR^a, -OC(O)N(R^a)₂, -C(O)N(R^a)₂, -N(R^a)C(O)OR^a, -N(R^a)C(O)R^a, -N(R^a)C(O)N(R^a)₂, N(R^a)C(NR^a)N(R^a)₂, -N(R^a)S(O)_tR^a (where *t* is 1 or 2), -S(O)_tOR^a (where *t* is 1 or 2), -S(O)_tN(R^a)₂ (where *t* is 1 or 2), or PO₃(R^a)₂ where each R^a is independently hydrogen, fluoroalkyl, carbocyclyl, carbocyclylalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Alkylaryl” refers to an -(alkyl)aryl radical where aryl and alkyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for aryl and alkyl respectively.

“Alkylhetaryl” refers to an -(alkyl)hetaryl radical where hetaryl and alkyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for aryl and alkyl respectively.

“Alkylheterocycloalkyl” refers to an -(alkyl) heterocyclyl radical where alkyl and heterocycloalkyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for heterocycloalkyl and alkyl respectively.

An “alkene” moiety refers to a group consisting of at least two carbon atoms and at least one carbon-carbon double bond, and an “alkyne” moiety refers to a group consisting of at least two carbon atoms and at least one carbon-carbon triple bond. The alkyl moiety, whether saturated or unsaturated, may be branched, straight chain, or cyclic.

“Alkenyl” refers to a straight or branched hydrocarbon chain radical group consisting solely of carbon and hydrogen atoms, containing at least one double bond, and having from two to ten carbon atoms (*i.e.*, (C₂₋₁₀)alkenyl or C₂₋₁₀ alkenyl). Whenever it appears herein, a numerical range such as “2 to 10” refers to each integer in the given range - *e.g.*, “2 to 10 carbon atoms” means that the alkenyl group may consist of 2 carbon atoms, 3 carbon atoms, *etc.*, up to and including 10 carbon atoms. The alkenyl moiety may be attached to the rest of the molecule by a single bond, such as for example, ethenyl (*i.e.*, vinyl), prop-1-enyl (*i.e.*, allyl), but-1-enyl, pent-1-enyl and penta-1,4-dienyl. Unless stated otherwise specifically in the specification, an alkenyl group is optionally substituted by one or more substituents which are independently alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, -OR^a, -SR^a, -OC(O)-R^a, -N(R^a)₂, -C(O)R^a, -C(O)OR^a, -OC(O)N(R^a)₂, -C(O)N(R^a)₂, -N(R^a)C(O)OR^a, -N(R^a)C(O)R^a, -N(R^a)C(O)N(R^a)₂, N(R^a)C(NR^a)N(R^a)₂, -N(R^a)S(O)_tR^a (where t is 1 or 2), -S(O)_tOR^a (where t is 1 or 2), -S(O)_tN(R^a)₂ (where t is 1 or 2), or PO₃(R^a)₂, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclylalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Alkenyl-cycloalkyl” refers to an -(alkenyl)cycloalkyl radical where alkenyl and cycloalkyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for alkenyl and cycloalkyl respectively.

“Alkynyl” refers to a straight or branched hydrocarbon chain radical group consisting solely of carbon and hydrogen atoms, containing at least one triple bond, having from two to ten carbon atoms (*i.e.*, (C₂₋₁₀)alkynyl or C₂₋₁₀ alkynyl). Whenever it appears herein, a numerical range such as “2 to 10” refers to each integer in the given range - *e.g.*, “2 to 10 carbon atoms” means that the alkynyl group may consist of 2 carbon atoms, 3 carbon atoms, *etc.*, up to and including 10 carbon atoms. The alkynyl may be attached to the rest of the molecule by a single bond, for example, ethynyl, propynyl, butynyl, pentynyl and hexynyl. Unless stated otherwise specifically in the specification, an alkynyl group is optionally substituted by one or more substituents which independently are: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, trifluoromethyl, trifluoromethoxy, nitro, trimethylsilanyl, -OR^a, -SR^a, -OC(O)-R^a, -N(R^a)₂, -C(O)R^a, -C(O)OR^a, -OC(O)N(R^a)₂, -C(O)N(R^a)₂, -N(R^a)C(O)OR^a, -N(R^a)C(O)R^a, -N(R^a)C(O)N(R^a)₂, N(R^a)C(NR^a)N(R^a)₂, -N(R^a)S(O)_tR^a (where t is 1 or 2), -S(O)_tOR^a (where t is 1 or 2), -S(O)_tN(R^a)₂ (where t is 1 or 2), or PO₃(R^a)₂, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Alkynyl-cycloalkyl” refers to an -(alkynyl)cycloalkyl radical where alkynyl and cycloalkyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for alkynyl and cycloalkyl respectively.

“Carboxaldehyde” refers to a -(C=O)H radical.

“Carboxyl” refers to a -(C=O)OH radical.

“Cyano” refers to a -CN radical.

“Cycloalkyl” refers to a monocyclic or polycyclic radical that contains only carbon and hydrogen, and may be saturated, or partially unsaturated. Cycloalkyl groups include groups having from 3 to 10 ring atoms (*i.e.*, (C₃₋₁₀)cycloalkyl or C₃₋₁₀ cycloalkyl). Whenever it appears herein, a numerical range such as “3 to 10” refers to each integer in the given range - *e.g.*, “3 to 10 carbon atoms” means that the cycloalkyl group may consist of 3 carbon atoms, *etc.*, up to and including 10 carbon atoms. Illustrative examples of cycloalkyl groups include, but are not limited to the following moieties: cyclopropyl, cyclobutyl, cyclopentyl, cyclopentenyl, cyclohexyl, cyclohexenyl,

cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, norbornyl, and the like. Unless stated otherwise specifically in the specification, a cycloalkyl group is optionally substituted by one or more substituents which independently are: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, $-OR^a$, $-SR^a$, $-OC(O)-R^a$, $-N(R^a)_2$, $-C(O)R^a$, $-C(O)OR^a$, $-OC(O)N(R^a)_2$, $-C(O)N(R^a)_2$, $-N(R^a)C(O)OR^a$, $-N(R^a)C(O)R^a$, $-N(R^a)C(O)N(R^a)_2$, $N(R^a)C(NR^a)N(R^a)_2$, $-N(R^a)S(O)_tR^a$ (where t is 1 or 2), $-S(O)_tOR^a$ (where t is 1 or 2), $-S(O)_tN(R^a)_2$ (where t is 1 or 2), or $PO_3(R^a)_2$, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Cycloalkyl-alkenyl” refers to a $-(cycloalkyl)alkenyl$ radical where cycloalkyl and alkenyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for cycloalkyl and alkenyl, respectively.

“Cycloalkyl-heterocycloalkyl” refers to a $-(cycloalkyl)heterocycloalkyl$ radical where cycloalkyl and heterocycloalkyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for cycloalkyl and heterocycloalkyl, respectively.

“Cycloalkyl-heteroaryl” refers to a $-(cycloalkyl)heteroaryl$ radical where cycloalkyl and heteroaryl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for cycloalkyl and heteroaryl, respectively.

The term “alkoxy” refers to the group $-O-alkyl$, including from 1 to 8 carbon atoms of a straight, branched, cyclic configuration and combinations thereof attached to the parent structure through an oxygen. Examples include, but are not limited to, methoxy, ethoxy, propoxy, isopropoxy, cyclopropyloxy and cyclohexyloxy. “Lower alkoxy” refers to alkoxy groups containing one to six carbons.

The term “substituted alkoxy” refers to alkoxy wherein the alkyl constituent is substituted (*i.e.*, $-O-(substituted\ alkyl)$). Unless stated otherwise specifically in the specification, the alkyl moiety of an alkoxy group is optionally substituted by one or more substituents which independently are: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo,

cyano, trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, $-OR^a$, $-SR^a$, $-OC(O)-R^a$, $-N(R^a)_2$, $-C(O)R^a$, $-C(O)OR^a$, $-OC(O)N(R^a)_2$, $-C(O)N(R^a)_2$, $-N(R^a)C(O)OR^a$, $-N(R^a)C(O)R^a$, $-N(R^a)C(O)N(R^a)_2$, $N(R^a)C(NR^a)N(R^a)_2$, $-N(R^a)S(O)_tR^a$ (where t is 1 or 2), $-S(O)_tOR^a$ (where t is 1 or 2), $-S(O)_tN(R^a)_2$ (where t is 1 or 2), or $PO_3(R^a)_2$, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

The term “alkoxycarbonyl” refers to a group of the formula (alkoxy)(C=O)- attached through the carbonyl carbon wherein the alkoxy group has the indicated number of carbon atoms. Thus a (C_{1-6}) alkoxycarbonyl group is an alkoxy group having from 1 to 6 carbon atoms attached through its oxygen to a carbonyl linker. “Lower alkoxycarbonyl” refers to an alkoxycarbonyl group wherein the alkoxy group is a lower alkoxy group.

The term “substituted alkoxycarbonyl” refers to the group (substituted alkyl)-O-C(O)- wherein the group is attached to the parent structure through the carbonyl functionality. Unless stated otherwise specifically in the specification, the alkyl moiety of an alkoxycarbonyl group is optionally substituted by one or more substituents which independently are: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, $-OR^a$, $-SR^a$, $-OC(O)-R^a$, $-N(R^a)_2$, $-C(O)R^a$, $-C(O)OR^a$, $-OC(O)N(R^a)_2$, $-C(O)N(R^a)_2$, $-N(R^a)C(O)OR^a$, $-N(R^a)C(O)R^a$, $-N(R^a)C(O)N(R^a)_2$, $N(R^a)C(NR^a)N(R^a)_2$, $-N(R^a)S(O)_tR^a$ (where t is 1 or 2), $-S(O)_tOR^a$ (where t is 1 or 2), $-S(O)_tN(R^a)_2$ (where t is 1 or 2), or $PO_3(R^a)_2$, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Acyl” refers to the groups (alkyl)-C(O)-, (aryl)-C(O)-, (heteroaryl)-C(O)-, (heteroalkyl)-C(O)- and (heterocycloalkyl)-C(O)-, wherein the group is attached to the parent structure through the carbonyl functionality. If the R radical is heteroaryl or heterocycloalkyl, the hetero ring or chain atoms contribute to the total number of chain or ring atoms. Unless stated otherwise specifically in the specification, the alkyl, aryl or heteroaryl moiety of the acyl group is optionally substituted by one or more substituents which are independently alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano,

trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, $-OR^a$, $-SR^a$, $-OC(O)-R^a$, $-N(R^a)_2$, $-C(O)R^a$, $-C(O)OR^a$, $-OC(O)N(R^a)_2$, $-C(O)N(R^a)_2$, $-N(R^a)C(O)OR^a$, $-N(R^a)C(O)R^a$, $-N(R^a)C(O)N(R^a)_2$, $N(R^a)C(NR^a)N(R^a)_2$, $-N(R^a)S(O)_tR^a$ (where t is 1 or 2), $-S(O)_tOR^a$ (where t is 1 or 2), $-S(O)_tN(R^a)_2$ (where t is 1 or 2), or $PO_3(R^a)_2$, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclylalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Acyloxy” refers to a $R(C=O)O-$ radical wherein R is alkyl, aryl, heteroaryl, heteroalkyl or heterocycloalkyl, which are as described herein. If the R radical is heteroaryl or heterocycloalkyl, the hetero ring or chain atoms contribute to the total number of chain or ring atoms. Unless stated otherwise specifically in the specification, the R of an acyloxy group is optionally substituted by one or more substituents which independently are: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, $-OR^a$, $-SR^a$, $-OC(O)-R^a$, $-N(R^a)_2$, $-C(O)R^a$, $-C(O)OR^a$, $-OC(O)N(R^a)_2$, $-C(O)N(R^a)_2$, $-N(R^a)C(O)OR^a$, $-N(R^a)C(O)R^a$, $-N(R^a)C(O)N(R^a)_2$, $N(R^a)C(NR^a)N(R^a)_2$, $-N(R^a)S(O)_tR^a$ (where t is 1 or 2), $-S(O)_tOR^a$ (where t is 1 or 2), $-S(O)_tN(R^a)_2$ (where t is 1 or 2), or $PO_3(R^a)_2$, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclylalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Acylsulfonamide” refers to a $-S(O)_2-N(R^a)-C(=O)-$ radical, where R^a is hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclylalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl. Unless stated otherwise specifically in the specification, an acylsulfonamide group is optionally substituted by one or more substituents which independently are: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, $-OR^a$, $-SR^a$, $-OC(O)-R^a$, $-N(R^a)_2$, $-C(O)R^a$, $-C(O)OR^a$, $-OC(O)N(R^a)_2$, $-C(O)N(R^a)_2$, $-N(R^a)C(O)OR^a$, $-N(R^a)C(O)R^a$, $-N(R^a)C(O)N(R^a)_2$, $N(R^a)C(NR^a)N(R^a)_2$, $-N(R^a)S(O)_tR^a$ (where t is 1 or 2), $-S(O)_tOR^a$ (where t is 1 or 2), $-S(O)_tN(R^a)_2$ (where t is 1 or 2), or $PO_3(R^a)_2$, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclylalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Amino” or “amine” refers to a $-N(R^a)_2$ radical group, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl, unless stated otherwise specifically in the specification. When a $-N(R^a)_2$ group has two R^a substituents other than hydrogen, they can be combined with the nitrogen atom to form a 4-, 5-, 6- or 7-membered ring. For example, $-N(R^a)_2$ is intended to include, but is not limited to, 1-pyrrolidinyl and 4-morpholinyl. Unless stated otherwise specifically in the specification, an amino group is optionally substituted by one or more substituents which independently are: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, $-OR^a$, $-SR^a$, $-OC(O)-R^a$, $-N(R^a)_2$, $-C(O)R^a$, $-C(O)OR^a$, $-OC(O)N(R^a)_2$, $-C(O)N(R^a)_2$, $-N(R^a)C(O)OR^a$, $-N(R^a)C(O)R^a$, $-N(R^a)C(O)N(R^a)_2$, $N(R^a)C(NR^a)N(R^a)_2$, $-N(R^a)S(O)_tR^a$ (where t is 1 or 2), $-S(O)_tOR^a$ (where t is 1 or 2), $-S(O)_tN(R^a)_2$ (where t is 1 or 2), or $PO_3(R^a)_2$, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

The term “substituted amino” also refers to N-oxides of the groups $-NHR^a$, and NR^aR^a each as described above. N-oxides can be prepared by treatment of the corresponding amino group with, for example, hydrogen peroxide or m-chloroperoxybenzoic acid.

“Amide” or “amido” refers to a chemical moiety with formula $-C(O)N(R)_2$ or $-NHC(O)R$, where R is selected from the group consisting of hydrogen, alkyl, cycloalkyl, aryl, heteroaryl (bonded through a ring carbon) and heteroalicyclic (bonded through a ring carbon), each of which moiety may itself be optionally substituted. The R_2 of $-N(R)_2$ of the amide may optionally be taken together with the nitrogen to which it is attached to form a 4-, 5-, 6- or 7-membered ring. Unless stated otherwise specifically in the specification, an amido group is optionally substituted independently by one or more of the substituents as described herein for alkyl, cycloalkyl, aryl, heteroaryl, or heterocycloalkyl. An amide may be an amino acid or a peptide molecule attached to a compound disclosed herein, thereby forming a prodrug. The procedures and specific groups to make such amides are known to those of skill in the art and can readily be

found in seminal sources such as Greene and Wuts, *Protective Groups in Organic Synthesis*, 3rd Ed., John Wiley & Sons, New York, N.Y., 1999, which is incorporated herein by reference in its entirety.

“Aromatic” or “aryl” or “Ar” refers to an aromatic radical with six to ten ring atoms (*e.g.*, C₆-C₁₀ aromatic or C₆-C₁₀ aryl) which has at least one ring having a conjugated pi electron system which is carbocyclic (*e.g.*, phenyl, fluorenyl, and naphthyl). Bivalent radicals formed from substituted benzene derivatives and having the free valences at ring atoms are named as substituted phenylene radicals. Bivalent radicals derived from univalent polycyclic hydrocarbon radicals whose names end in “-yl” by removal of one hydrogen atom from the carbon atom with the free valence are named by adding “-idene” to the name of the corresponding univalent radical, *e.g.*, a naphthyl group with two points of attachment is termed naphthylidene. Whenever it appears herein, a numerical range such as “6 to 10” refers to each integer in the given range; *e.g.*, “6 to 10 ring atoms” means that the aryl group may consist of 6 ring atoms, 7 ring atoms, *etc.*, up to and including 10 ring atoms. The term includes monocyclic or fused-ring polycyclic (*i.e.*, rings which share adjacent pairs of ring atoms) groups. Unless stated otherwise specifically in the specification, an aryl moiety is optionally substituted by one or more substituents which are independently alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, -OR^a, -SR^a, -OC(O)-R^a, -N(R^a)₂, -C(O)R^a, -C(O)OR^a, -OC(O)N(R^a)₂, -C(O)N(R^a)₂, -N(R^a)C(O)OR^a, -N(R^a)C(O)R^a, -N(R^a)C(O)N(R^a)₂, N(R^a)C(NR^a)N(R^a)₂, -N(R^a)S(O)_tR^a (where t is 1 or 2), -S(O)_tOR^a (where t is 1 or 2), -S(O)_tN(R^a)₂ (where t is 1 or 2), or PO₃(R^a)₂, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

The term “aryloxy” refers to the group -O-aryl.

The term “substituted aryloxy” refers to aryloxy wherein the aryl substituent is substituted (*i.e.*, -O-(substituted aryl)). Unless stated otherwise specifically in the specification, the aryl moiety of an aryloxy group is optionally substituted by one or more substituents which independently are: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano,

trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, $-OR^a$, $-SR^a$, $-OC(O)-R^a$, $-N(R^a)_2$, $-C(O)R^a$, $-C(O)OR^a$, $-OC(O)N(R^a)_2$, $-C(O)N(R^a)_2$, $-N(R^a)C(O)OR^a$, $-N(R^a)C(O)R^a$, $-N(R^a)C(O)N(R^a)_2$, $N(R^a)C(NR^a)N(R^a)_2$, $-N(R^a)S(O)_tR^a$ (where t is 1 or 2), $-S(O)_tOR^a$ (where t is 1 or 2), $-S(O)_tN(R^a)_2$ (where t is 1 or 2), or $PO_3(R^a)_2$, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclylalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Aralkyl” or “arylalkyl” refers to an (aryl)alkyl-radical where aryl and alkyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for aryl and alkyl respectively.

“Ester” refers to a chemical radical of formula $-COOR$, where R is selected from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl (bonded through a ring carbon) and heteroalicyclic (bonded through a ring carbon). The procedures and specific groups to make esters are known to those of skill in the art and can readily be found in seminal sources such as Greene and Wuts, *Protective Groups in Organic Synthesis*, 3rd Ed., John Wiley & Sons, New York, N.Y., 1999, which is incorporated herein by reference in its entirety. Unless stated otherwise specifically in the specification, an ester group is optionally substituted by one or more substituents which independently are: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, trifluoromethyl, trifluoromethoxy, nitro, trimethylsilyl, $-OR^a$, $-SR^a$, $-OC(O)-R^a$, $-N(R^a)_2$, $-C(O)R^a$, $-C(O)OR^a$, $-OC(O)N(R^a)_2$, $-C(O)N(R^a)_2$, $-N(R^a)C(O)OR^a$, $-N(R^a)C(O)R^a$, $-N(R^a)C(O)N(R^a)_2$, $N(R^a)C(NR^a)N(R^a)_2$, $-N(R^a)S(O)_tR^a$ (where t is 1 or 2), $-S(O)_tOR^a$ (where t is 1 or 2), $-S(O)_tN(R^a)_2$ (where t is 1 or 2), or $PO_3(R^a)_2$, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclylalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Fluoroalkyl” refers to an alkyl radical, as defined above, that is substituted by one or more fluoro radicals, as defined above, for example, trifluoromethyl, difluoromethyl, 2,2,2-trifluoroethyl, 1-fluoromethyl-2-fluoroethyl, and the like. The alkyl part of the fluoroalkyl radical may be optionally substituted as defined above for an alkyl group.

“Halo,” “halide,” or, alternatively, “halogen” is intended to mean fluoro, chloro, bromo or iodo. The terms “haloalkyl,” “haloalkenyl,” “haloalkynyl,” and “haloalkoxy” include alkyl, alkenyl, alkynyl and alkoxy structures that are substituted with one or more halo groups or with combinations thereof. For example, the terms “fluoroalkyl” and “fluoroalkoxy” include haloalkyl and haloalkoxy groups, respectively, in which the halo is fluorine.

“Heteroalkyl,” “heteroalkenyl,” and “heteroalkynyl” refer to optionally substituted alkyl, alkenyl and alkynyl radicals and which have one or more skeletal chain atoms selected from an atom other than carbon, *e.g.*, oxygen, nitrogen, sulfur, phosphorus or combinations thereof. A numerical range may be given - *e.g.*, C₁-C₄ heteroalkyl which refers to the chain length in total, which in this example is 4 atoms long. A heteroalkyl group may be substituted with one or more substituents which independently are: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, nitro, oxo, thioxo, trimethylsilanyl, -OR^a, -SR^a, -OC(O)-R^a, -N(R^a)₂, -C(O)R^a, -C(O)OR^a, -OC(O)N(R^a)₂, -C(O)N(R^a)₂, -N(R^a)C(O)OR^a, -N(R^a)C(O)R^a, -N(R^a)C(O)N(R^a)₂, N(R^a)C(NR^a)N(R^a)₂, -N(R^a)S(O)_tR^a (where t is 1 or 2), -S(O)_tOR^a (where t is 1 or 2), -S(O)_tN(R^a)₂ (where t is 1 or 2), or PO₃(R^a)₂, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Heteroalkylaryl” refers to an -(heteroalkyl)aryl radical where heteroalkyl and aryl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for heteroalkyl and aryl, respectively.

“Heteroalkylheteroaryl” refers to an -(heteroalkyl)heteroaryl radical where heteroalkyl and heteroaryl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for heteroalkyl and heteroaryl, respectively.

“Heteroalkylheterocycloalkyl” refers to an -(heteroalkyl)heterocycloalkyl radical where heteroalkyl and heterocycloalkyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for heteroalkyl and heterocycloalkyl, respectively.

“Heteroalkylcycloalkyl” refers to an -(heteroalkyl)cycloalkyl radical where heteroalkyl and cycloalkyl are as disclosed herein and which are optionally substituted by one or more of the substituents described as suitable substituents for heteroalkyl and cycloalkyl, respectively.

“Heteroaryl” or “heteroaromatic” or “HetAr” refers to a 5- to 18-membered aromatic radical (*e.g.*, C₅-C₁₃ heteroaryl) that includes one or more ring heteroatoms selected from nitrogen, oxygen and sulfur, and which may be a monocyclic, bicyclic, tricyclic or tetracyclic ring system. Whenever it appears herein, a numerical range such as “5 to 18” refers to each integer in the given range - *e.g.*, “5 to 18 ring atoms” means that the heteroaryl group may consist of 5 ring atoms, 6 ring atoms, etc., up to and including 18 ring atoms. Bivalent radicals derived from univalent heteroaryl radicals whose names end in “-yl” by removal of one hydrogen atom from the atom with the free valence are named by adding “-idene” to the name of the corresponding univalent radical - *e.g.*, a pyridyl group with two points of attachment is a pyridylidene. A N-containing “heteroaromatic” or “heteroaryl” moiety refers to an aromatic group in which at least one of the skeletal atoms of the ring is a nitrogen atom. The polycyclic heteroaryl group may be fused or non-fused. The heteroatom(s) in the heteroaryl radical are optionally oxidized. One or more nitrogen atoms, if present, are optionally quaternized. The heteroaryl may be attached to the rest of the molecule through any atom of the ring(s). Examples of heteroaryls include, but are not limited to, azepinyl, acridinyl, benzimidazolyl, benzindolyl, 1,3-benzodioxolyl, benzofuranyl, benzooxazolyl, benzo[*d*]thiazolyl, benzothiadiazolyl, benzo[*b*][1,4]dioxepinyl, benzo[*b*][1,4]oxazinyl, 1,4-benzodioxanyl, benzonaphthofuranyl, benzoxazolyl, benzodioxolyl, benzodioxinyl, benzoxazolyl, benzopyranyl, benzopyranonyl, benzofuranyl, benzofuranonyl, benzofurazanyl, benzothiazolyl, benzothienyl(benzothiophenyl), benzothieno[3,2-*d*]pyrimidinyl, benzotriazolyl, benzo[4,6]imidazo[1,2-*a*]pyridinyl, carbazolyl, cinnolinyl, cyclopenta[*d*]pyrimidinyl, 6,7-dihydro-5*H*-cyclopenta[4,5]thieno[2,3-*d*]pyrimidinyl, 5,6-dihydrobenzo[*h*]quinazolinyl, 5,6-dihydrobenzo[*h*]cinnolinyl, 6,7-dihydro-5*H*-benzo[6,7]cyclohepta[1,2-*c*]pyridazinyl, dibenzofuranyl, dibenzothiophenyl, furanyl, furazanyl, furanonyl, furo[3,2-*c*]pyridinyl, 5,6,7,8,9,10-hexahydrocycloocta[*d*]pyrimidinyl, 5,6,7,8,9,10-hexahydrocycloocta[*d*]pyridazinyl,

5,6,7,8,9,10-hexahydrocycloocta[*d*]pyridinyl, isothiazolyl, imidazolyl, indazolyl, indolyl, indazolyl, isoindolyl, indolinyl, isoindolinyl, isoquinolyl, indoliziny, isoxazolyl, 5,8-methano-5,6,7,8-tetrahydroquinazoliny, naphthyridinyl, 1,6-naphthyridinonyl, oxadiazolyl, 2-oxoazepinyl, oxazolyl, oxiranyl, 5,6,6a,7,8,9,10,10a-octahydrobenzo[*h*]quinazoliny, 1-phenyl-1*H*-pyrrolyl, phenazinyl, phenothiazinyl, phenoxazinyl, phthalazinyl, pteridinyl, purinyl, pyranyl, pyrrolyl, pyrazolyl, pyrazolo[3,4-*d*]pyrimidinyl, pyridinyl, pyrido[3,2-*d*]pyrimidinyl, pyrido[3,4-*d*]pyrimidinyl, pyrazinyl, pyrimidinyl, pyridazinyl, pyrrolyl, quinazoliny, quinoxalinyl, quinolinyl, isoquinolinyl, tetrahydroquinolinyl, 5,6,7,8-tetrahydroquinazoliny, 5,6,7,8-tetrahydrobenzo[4,5]thieno[2,3-*d*]pyrimidinyl, 6,7,8,9-tetrahydro-5*H*-cyclohepta[4,5]thieno[2,3-*d*]pyrimidinyl, 5,6,7,8-tetrahydropyrido[4,5-*c*]pyridazinyl, thiazolyl, thiadiazolyl, thiapyranyl, triazolyl, tetrazolyl, triazinyl, thieno[2,3-*d*]pyrimidinyl, thieno[3,2-*d*]pyrimidinyl, thieno[2,3-*c*]pyridinyl, and thiophenyl (*i.e.*, thienyl). Unless stated otherwise specifically in the specification, a heteroaryl moiety is optionally substituted by one or more substituents which are independently: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, nitro, oxo, thio, trimethylsilyl, -OR^a, -SR^a, -OC(O)R^a, -N(R^a)₂, -C(O)R^a, -C(O)OR^a, -OC(O)N(R^a)₂, -C(O)N(R^a)₂, -N(R^a)C(O)OR^a, -N(R^a)C(O)R^a, -N(R^a)C(O)N(R^a)₂, N(R^a)C(NR^a)N(R^a)₂, -N(R^a)S(O)_tR^a (where *t* is 1 or 2), -S(O)_tOR^a (where *t* is 1 or 2), -S(O)_tN(R^a)₂ (where *t* is 1 or 2), or PO₃(R^a)₂, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

Substituted heteroaryl also includes ring systems substituted with one or more oxide (-O-) substituents, such as, for example, pyridinyl N-oxides.

“Heteroarylalkyl” refers to a moiety having an aryl moiety, as described herein, connected to an alkylene moiety, as described herein, wherein the connection to the remainder of the molecule is through the alkylene group.

“Heterocycloalkyl” refers to a stable 3- to 18-membered non-aromatic ring radical that comprises two to twelve carbon atoms and from one to six heteroatoms selected from nitrogen, oxygen and sulfur. Whenever it appears herein, a numerical range such as “3 to 18” refers to each integer in the given range - *e.g.*, “3 to 18 ring atoms” means that the

heterocycloalkyl group may consist of 3 ring atoms, 4 ring atoms, *etc.*, up to and including 18 ring atoms. Unless stated otherwise specifically in the specification, the heterocycloalkyl radical is a monocyclic, bicyclic, tricyclic or tetracyclic ring system, which may include fused or bridged ring systems. The heteroatoms in the heterocycloalkyl radical may be optionally oxidized. One or more nitrogen atoms, if present, are optionally quaternized. The heterocycloalkyl radical is partially or fully saturated. The heterocycloalkyl may be attached to the rest of the molecule through any atom of the ring(s). Examples of such heterocycloalkyl radicals include, but are not limited to, dioxolanyl, thienyl[1,3]dithianyl, decahydroisoquinolyl, imidazolynyl, imidazolidinyl, isothiazolidinyl, isoxazolidinyl, morpholynyl, octahydroindolyl, octahydroisoindolyl, 2-oxopiperazinyl, 2-oxopiperidinyl, 2-oxopyrrolidinyl, oxazolidinyl, piperidinyl, piperazinyl, 4-piperidonyl, pyrrolidinyl, pyrazolidinyl, quinuclidinyl, thiazolidinyl, tetrahydrofuryl, trithianyl, tetrahydropyranyl, thiomorpholynyl, thiomorpholinyl, 1-oxo-thiomorpholynyl, and 1,1-dioxo-thiomorpholynyl. Unless stated otherwise specifically in the specification, a heterocycloalkyl moiety is optionally substituted by one or more substituents which independently are: alkyl, heteroalkyl, alkenyl, alkynyl, cycloalkyl, heterocycloalkyl, aryl, arylalkyl, heteroaryl, heteroarylalkyl, hydroxy, halo, cyano, nitro, oxo, thiooxo, trimethylsilanyl, $-OR^a$, $-SR^a$, $-OC(O)-R^a$, $-N(R^a)_2$, $-C(O)R^a$, $-C(O)OR^a$, $-OC(O)N(R^a)_2$, $-C(O)N(R^a)_2$, $-N(R^a)C(O)OR^a$, $-N(R^a)C(O)R^a$, $-N(R^a)C(O)N(R^a)_2$, $N(R^a)C(NR^a)N(R^a)_2$, $-N(R^a)S(O)_tR^a$ (where t is 1 or 2), $-S(O)_tOR^a$ (where t is 1 or 2), $-S(O)_tN(R^a)_2$ (where t is 1 or 2), or $PO_3(R^a)_2$, where each R^a is independently hydrogen, alkyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl or heteroarylalkyl.

“Heterocycloalkyl” also includes bicyclic ring systems wherein one non-aromatic ring, usually with 3 to 7 ring atoms, contains at least 2 carbon atoms in addition to 1-3 heteroatoms independently selected from oxygen, sulfur, and nitrogen, as well as combinations comprising at least one of the foregoing heteroatoms; and the other ring, usually with 3 to 7 ring atoms, optionally contains 1-3 heteroatoms independently selected from oxygen, sulfur, and nitrogen and is not aromatic.

“Nitro” refers to the $-NO_2$ radical.

“Oxa” refers to the -O- radical.

“Oxo” refers to the =O radical.

“Isomers” are different compounds that have the same molecular formula.

“Stereoisomers” are isomers that differ only in the way the atoms are arranged in space - *i.e.*, having a different stereochemical configuration. “Enantiomers” are a pair of stereoisomers that are non-superimposable mirror images of each other. A 1:1 mixture of a pair of enantiomers is a “racemic” mixture. The term “(±)” is used to designate a racemic mixture where appropriate. “Diastereoisomers” are stereoisomers that have at least two asymmetric atoms, but which are not mirror-images of each other. The absolute stereochemistry is specified according to the Cahn-Ingold-Prelog R-S system. When a compound is a pure enantiomer the stereochemistry at each chiral carbon can be specified by either (*R*) or (*S*). Resolved compounds whose absolute configuration is unknown can be designated (+) or (-) depending on the direction (dextro- or levorotatory) which they rotate plane polarized light at the wavelength of the sodium D line. Certain of the compounds described herein contain one or more asymmetric centers and can thus give rise to enantiomers, diastereomers, and other stereoisomeric forms that can be defined, in terms of absolute stereochemistry, as (*R*) or (*S*). The present chemical entities, pharmaceutical compositions and methods are meant to include all such possible isomers, including racemic mixtures, optically pure forms and intermediate mixtures. Optically active (*R*)- and (*S*)-isomers can be prepared using chiral synthons or chiral reagents, or resolved using conventional techniques. When the compounds described herein contain olefinic double bonds or other centers of geometric asymmetry, and unless specified otherwise, it is intended that the compounds include both *E* and *Z* geometric isomers. “Substituted” means that the referenced group may have attached one or more additional groups, radicals or moieties individually and independently selected from, for example, acyl, alkyl, alkylaryl, cycloalkyl, aralkyl, aryl, carbohydrate, carbonate, heteroaryl, heterocycloalkyl, hydroxy, alkoxy, aryloxy, mercapto, alkylthio, arylthio, cyano, halo, carbonyl, ester, thiocarbonyl, isocyanato, thiocyanato, isothiocyano, nitro, oxo, perhaloalkyl, perfluoroalkyl, phosphate, silyl, sulfinyl, sulfonyl, sulfonamidyl, sulfoxyl, sulfonate, urea, and amino, including mono- and di-substituted amino groups, and protected derivatives thereof. The substituents themselves may be substituted, for

example, a cycloalkyl substituent may itself have a halide substituent at one or more of its ring carbons. The term “optionally substituted” means optional substitution with the specified groups, radicals or moieties.

“Sulfanyl” refers to groups that include -S-(optionally substituted alkyl), -S-(optionally substituted aryl), -S-(optionally substituted heteroaryl) and -S-(optionally substituted heterocycloalkyl).

“Sulfinyl” refers to groups that include -S(O)-H, -S(O)-(optionally substituted alkyl), -S(O)-(optionally substituted amino), -S(O)-(optionally substituted aryl), -S(O)-(optionally substituted heteroaryl) and -S(O)-(optionally substituted heterocycloalkyl).

“Sulfonyl” refers to groups that include -S(O₂)-H, -S(O₂)-(optionally substituted alkyl), -S(O₂)-(optionally substituted amino), -S(O₂)-(optionally substituted aryl), -S(O₂)-(optionally substituted heteroaryl), and -S(O₂)-(optionally substituted heterocycloalkyl).

“Sulfonamidyl” or “sulfonamido” refers to a -S(=O)₂-NRR radical, where each R is selected independently from the group consisting of hydrogen, alkyl, cycloalkyl, aryl, heteroaryl (bonded through a ring carbon) and heteroalicyclic (bonded through a ring carbon). The R groups in -NRR of the -S(=O)₂-NRR radical may be taken together with the nitrogen to which it is attached to form a 4-, 5-, 6- or 7-membered ring. A sulfonamido group is optionally substituted by one or more of the substituents described for alkyl, cycloalkyl, aryl, heteroaryl, respectively.

“Sulfoxyl” refers to a -S(=O)₂OH radical.

“Sulfonate” refers to a -S(=O)₂-OR radical, where R is selected from the group consisting of alkyl, cycloalkyl, aryl, heteroaryl (bonded through a ring carbon) and heteroalicyclic (bonded through a ring carbon). A sulfonate group is optionally substituted on R by one or more of the substituents described for alkyl, cycloalkyl, aryl, heteroaryl, respectively.

In some embodiments, a chemical agent may be applied to a textile to be coated prior to providing a silk fibroin fragments coating. In some embodiments, a chemical agent may be applied to a textile after such textile has been coated with a silk fibroin fragments coating. One or more chemical agents may be applied, as set forth above, and may include a first chemical agent, second chemical agent, third chemical agent, and the like, where the chemical agents may be the same or a combination of two or more of the

chemical agents described herein. In some embodiments, chemical agents may provide selected properties to coated textile (e.g., fabric) including, but not limited to, an antimicrobial property, a water repellant property, an oil repellant property, a coloring property, a flame retardant property, a fabric softening property, a pH adjusting property, an anticrocking property, an antipilling property, and/or an antifelting property. Such chemical agents may include, but are not limited to, softeners (e.g., silicone), acidic agents, antimicrobials, finishing agents including monomers such as melted polyester, or combinations thereof. Chemical agents have been described in U.S. Patent Application Publications Nos. 20160222579, 20160281294, and 20190003113, all of which are incorporated herein in their entireties. Any chemical agent described herein may act as a precursor linker. In some embodiments, a precursor linker reacts with a substrate, and then fibroin can react with the linker. In some embodiments, a precursor linker reacts with silk fibroin, and then the substrate can react with the linker.

In some embodiments, the chemical agent may include one or more of a silicone, an acidic agent, a dyeing agent, a pigment dye, a traditional finishing agent, and a technical finishing agent. The dyeing agent may include one or more of a dispersing agent, a levelling agent, a fixing agent, a special resin, an antireducing agent, and an anticreasing agent. The pigment dye may include one or more of an antimigrating agent, a binding agent, an all in one agent, and a delave agent. The traditional finishing agent may include one or more of a wrinkle free treatment, a softener, a handle modifier, a waterborne polyurethanes dispersion, and other resins. The technical finishing agent may include one or more of a waterborne polyurethanes dispersion, an oil repellant, a water repellant, a crosslinker, and a thickener.

In some embodiments, the chemical agent may include an acidic agent. In some embodiments, an acidic agent may be a Brønsted acid. In an embodiment, the acidic agent includes one or more of citric acid and acetic acid. In an embodiment, the acidic agent aids the deposition and coating of silk fibroin fragments mixtures on the textile to be coated as compared to the absence of such acidic agent. In an embodiment, the acidic agent improves crystallization of the SPF mixtures at the textile to be coated.

In an embodiment, the acidic agent is added at a concentration by weight (% w/w or % w/v) or by volume (v/v) of greater than about 0.001 % , or greater than about 0.002

%, or greater than about 0.003 %, or greater than about 0.004 %, or greater than about 0.005 %, or greater than about 0.006 %, or greater than about 0.007 %, or greater than about 0.008 %, or greater than about 0.009 %, or greater than about 0.01 %, or greater than about 0.02 %, or greater than about 0.03 %, or greater than about 0.04 %, or greater than about 0.05 %, or greater than about 0.06 %, or greater than about 0.07 %, or greater than about 0.08 %, or greater than about 0.09 %, or greater than about 0.1 %, or greater than about 0.2 %, or greater than about 0.3 %, or greater than about 0.4 %, or greater than about 0.5 %, or greater than about 0.6 %, or greater than about 0.7 %, or greater than about 0.8 %, or greater than about 0.9 %, or greater than about 1.0 % or greater than about 2.0 %, or greater than about 3.0 %, or greater than about 4.0 %, or greater than about 5.0% .

In an embodiment, the acidic agent is added at a concentration by weight (% w/w or % w/v) or by volume (v/v) of less than about 0.001 %, or less than about 0.002 %, or less than about 0.003 %, or less than about 0.004 % , or less than about 0.005 %, or less than about 0.006 %, or less than about 0.007 %, or less than about 0.008 %, or less than about 0.009 %, or less than about 0.01 %, or less than about 0.02 %, or less than about 0.03 %, or less than about 0.04 %, or less than about 0.05 %, or less than about 0.06 %, or less than about 0.07 %, or less than about 0.08 %, or less than about 0.09 %, or less than about 0.1 %, or less than about 0.2 %, or less than about 0.3 %, or less than about 0.4 %, or less than about 0.5 %, or less than about 0.6%, or less than about 0.7 %, or less than about 0.8 %, or less than about 0.9 %, or less than about 1.0 % or less than about 2.0 %, or less than about 3.0 %, or less than about 4.0 %, or less than about 5.0 %.

In some embodiments, a composition including silk fibroin fragments may have a pH of less than about 9, or less than about 8.5, or less than about 8, or less than about 7.5, or less than about 7, or less than about 6.5, or less than about 6, or less than about 5.5, or less than about 5, or less than about 4.5, or less than about 4, or greater than about 3.5, or greater than about 4, or greater than about 4.5, or greater than about 5, or greater than about 5.5, or greater than about 6, or greater than about 6.5, or greater than about 7, or greater than about 7.5, or greater than about 8, or greater than about 8.5.

In some embodiments, a composition including silk fibroin fragments may include an acidic agent, and may have a pH of less than about 9, or less than about 8.5, or

less than about 8, or less than about 7.5, or less than about 7, or less than about 6.5, or less than about 6, or less than about 5.5, or less than about 5, or less than about 4.5, or less than about 4, or greater than about 3.5, or greater than about 4, or greater than about 4.5, or greater than about 5, or greater than about 5.5, or greater than about 6, or greater than about 6.5, or greater than about 7, or greater than about 7.5, or greater than about 8, or greater than about 8.5.

In an embodiment, the chemical agent may include silicone. In some embodiments, a SFS may include silicone. In some embodiments, silicone may include a silicone emulsion. The term “silicone,” may generally refer to a broad family of synthetic polymers, mixtures of polymers, and/or emulsions thereof, that have a repeating silicon-oxygen backbone including, but not limited to, polysiloxanes. For example, a silicone may include ULTRATEX® CSP, which is a commercially available (Huntsman International LLC) silicone emulsion that may be used as a softening agent and which may also increase fabric resilience, elasticity of knitted fabrics, and fiber lubrication and also improve sewability. A silicone may also include ULTRATEX® CI, which is a commercially available silicone composition (Huntsman International LLC) that may be used as a fabric softening agent.

In some embodiments, a composition including silk fibroin fragments may include silicone in a concentration by weight (% w/w or % w/v) or by volume (v/v) of less than about 25 %, or less than about 20 %, or less than about 15 %, or less than about 10 %, or less than about 9 %, or less than about 8 %, or less than about 7 %, or less than about 6 %, or less than about 5 %, or less than about 4 %, or less than about 3 %, or less than about 2 %, or less than about 1 %, or less than about 0.9 %, or less than about 0.8%, or less than about 0.7%, or less than about 0.6 %, or less than about 0.5%, or less than about 0.4%, or less than about 0.3%, or less than about 0.2%, or less than about 0.1%, or less than about 0.01%, or less than about 0.001 %.

In some embodiments, a composition including silk fibroin fragments may include silicone in a concentration by weight (% w/w or % w/v) or by volume (v/v) of greater than about 25 %, or greater than about 20 %, or greater than about 15 %, or greater than about 10 %, or greater than about 9 %, or greater than about 8 %, or greater than about 7 %, or greater than about 6 %, or greater than about 5 %, or greater than

about 4 %, or greater than about 3 %, or greater than about 2 %, or greater than about 1 %, or greater than about 0.9 %, or greater than about 0.8%, or greater than about 0.7%, or greater than about 0.6 %, or greater than about 0.5%, or greater than about 0.4%, or greater than about 0.3%, or greater than about 0.2%, or greater than about 0.1%, or greater than about 0.01%, or greater than about 0.001 %.

In some embodiments, a composition including silk fibroin fragments may be supplied in a concentrated form suspended in water. In some embodiments, a composition including silk fibroin fragments may have a concentration by weight (% w/w or % w/v) or by volume (v/v) of less than about 50 %, or less than about 45%, or less than about 40%, or less than about 35%, or less than about 30%, or less than about 25%, or less than about 20%, or less than about 15%, or less than about 10%, or less than about 5%, or less than about 4%, or less than about 3%, or less than about 2%, or less than about 1%, or less than about 0.1%, or less than about 0.01%, or less than about 0.001%, or less than about 0.0001%, or less than about 0.00001%. In some embodiments, a composition including silk fibroin fragments may have a concentration by weight (% w/w or % w/v) or by volume (v/v) of greater than about 50 %, or greater than about 45%, or greater than about 40%, or greater than about 35%, or greater than about 30%, or greater than about 25%, or greater than about 20%, or greater than about 15%, or greater than about 10%, or greater than about 5%, or greater than about 4%, or greater than about 3%, or greater than about 2%, or greater than about 1%, or greater than about 0.1%, or greater than about 0.01%, or greater than about 0.001%, or greater than about 0.0001%, or greater than about 0.00001%.

In some embodiments, the coating processes of the disclosure may include a finishing step for the resulting coated textiles. In some embodiments, the finishing or final finishing of the textiles (e.g., fabrics) that are coated with a composition including silk fibroin fragments under the processes disclosed herein may include sueding, steaming, brushing, polishing, compacting, raising, tigering, shearing, heatsetting, waxing, air jet, calendaring, pressing, shrinking, treatment with polymerizer, coating, lamination, and/or laser etching. In some embodiments, finishing of the silk fibroin fragments coated textiles may include treatment of the textiles with an AIRO® 24 dryer

that may be used for continuous and open-width tumbling treatments of woven, non-woven, and knitted fabrics.

In some embodiments, the coated textiles (e.g., fabrics) described herein may meet or exceed requirements established by the following Test Methods:

<u>Test Description</u>	<u>Test Method</u>	<u>Requirements</u>
Dimensional Stability to Laundering	AATCC 135	Maximum, Length: -3%, Width: -3% Maximum, Length: -3%, Width: -5%, for twoway Stretch Fabrics Maximum, Length: -5%, Width: -5%, for fourway Stretch Fabrics No Growth
Dimensional Stability to Dry Cleaning	AATCC 158	Maximum, Length: -3%, Width: -3% Maximum, Length: -3%, Width: -5%, for twoway Stretch Fabrics Maximum, Length: -5%, Width: -5%, for fourway Stretch Fabrics No Growth
Pilling Resistance	ASTM D 3512	Minimum 3.0
Abrasion Resistance	ASTM D 4966	No rupture to 10,000 cycles (plain fabrics up to 7.5 oz/yd ² ; or no rupture to 15,000 cycles (plain fabrics over 7.5 oz/yd ²)
Tearing Strength	ASTM D 1424	Shorts, Pants, Jeans, Jackets, All Plus Size Styles: 2.5 Lbs Minimum; or Blouse, Skirt Dress, Lining, excluding plus size styles: 1.5 Lbs Minimum; or

		Intimate: <3 oz/yd ² : Minimum 1.5lbs; 3~6oz/yd ² : Minimum 2.0lbs >6 oz/yd ² : Minimum 2.5lbs
Colorfastness to Laundering/Colorfastness to Washing	AATCC 61, 2A	Color Change: Minimum 4.0 Staining: Minimum 3.0
Colorfastness to Dry Cleaning	AATCC 132	Color Change: Minimum 4.0 Staining: Minimum 3.0
Colorfastness to Crocking/Colorfastness to Rubbing	AATCC 8	All except below - Dry: Minimum 4.0; Wet: Minimum 3.0; or Dark Shades (black, red, navy) - Dry: Minimum 4.0; Wet: Minimum 2.5; or Indigos - Dry: Minimum 3.0; Wet: Minimum 2.0; or Pigments - Dry: Minimum 3.5; Wet: Minimum 2.5.
Colorfastness to Water	AATCC 107	Color Change: Minimum 4.0; Staining: Minimum 3.0
Colorfastness to Perspiration	AATCC 15	Color Change: Minimum 4.0; Staining: Minimum 3
Colorfastness to Light	AATCC 16/20 AFU AATCC 16/5 AFU	Color Change: Minimum 4.0
pH Value	AATCC 81	4.0 ~ 8.5 or 4.0~7.5 (children < 36 months)
Antimicrobial	AATCC 147 AATCC 100 ASTM E 2149	Original: 0% Bacterial Growth 20 Washes: 0% Bacterial Growth Minimum 99.9% Reduction Original: Minimum 99.9% Reduction 20 Washes: Minimum 80% Reduction
Wicking	AATCC 79	1.0 second or less

Water Repellency – Spray Test	AATCC 22	Original: 100 Rating After 3x Washes: Minimum 70 Rating
Water Resistance – Rain Test	AATCC 35	Maximum 1 gram on original and after 3 x washes
Dimensional Stability to Laundering (Yoga Garment)	AATCC 150	Maximum, Length= - 3%, Width= -3% Maximum, Length= -3%, Width= -5% for two-way Stretch Fabrics Maximum, Length= -5%, Width= -5% for four-way Stretch fabrics No Distortion Between Components No Growth
Dimensional Stability to Dry Cleaning (Yoga Garment)	AATCC 158	Maximum, Length= -3%, Width= -3% Maximum, Length= -3%, Width= -5%, for two-way Stretch Fabrics Maximum, Length= -5%, Width= -5%, for four-way Stretch Fabrics No Distortion Between Components No Growth
Pilling Resistance (Yoga Garment)	ASM D 3512	Minimum 3.0
Colorfastness to Laundering/Colorfastness to Washing (Yoga Garment)	AATCC 61, 2A	Color Change: Minimum 4.0 Staining: Minimum 3.0
Colorfastness Crocking/Colorfastness to Rubbing (Yoga Garment)	AATCC 8	General: Dry: Minimum 4.0 ; Wet: Minimum 3.0; For Dark Colors (Black, Red, Navy): Wet: Minimum 2.5

		Pigment: Dry: Minimum 3.5 ; Wet: Minimum 2.5 Indigos: Dry: Minimum 3.0; Wet: Minimum 2.0
Colorfastness to Water (Yoga Garment)	AATCC 107	Color Change: Minimum 4.0 Staining: Minimum 3.0
Colorfastness to Perspiration (Yoga Garment)	AATCC 15	Color Change: 4.0 or better Staining: 3.0 or better
Colorfastness to Light (Yoga Garment)	AATCC 16, 20 AFU/5 AFU	Minimum 4.0, All, Except Silk/ Minimum 4.0, Silk
pH Value (Yoga Garment)	AATCC 81	Children (>36 months) & Adults: 4.0 ~ 8.5 Children (< 36 months): 4.0 ~ 7.5

In some embodiments, the coated textiles (e.g., fabrics) described herein may meet requirements established by the foregoing Test Methods. In some embodiments, the coated textiles (e.g., fabrics) described herein may exceed the requirements established by the foregoing Test Methods.

In some embodiments, the coated textiles (e.g., fabrics) may have antimicrobial (e.g., antifungal and/or antibacterial activity) due to the silk fibroin fragments coating. In an embodiment, antibacterial activity may be determined by the ability of bacteria on the coated textile's surface to be washed away from the coated textile surface following one or more wash cycles, or two or more wash cycles, or three or more wash cycles, or four or more wash cycles, or five or more wash cycles, where the bacteria do not adhere to the surface of the coated textile. In an embodiment, antibacterial activity may be determined by the ability of the coating to reduce the quantity of the bacteria deposited on a surface of the coated textile, wherein the coating may reduce the quantity of the bacteria by greater than about 1%, or greater than about 2%, or greater than about 3%, or greater than about 4%, or greater than about 5%, or greater than about 10%, or greater than about 20%, or greater than about 30%, or greater than about 40%, or greater than about 50%, or greater than about 60%, or greater than about 70%, or greater than about 80%, or greater than about 90%, or greater than about 95%, or greater than about 96%, or greater than

about 97%, or greater than about 98%, or greater than about 99%, or by about 100%. In an embodiment, antibacterial activity of the coating on the coated textile may be determined by fluorescent activity (see, e.g., U.S. Patent Nos. 5,089,395 and 5,968,762, the entirety of which are incorporated herein by reference). In an embodiment, antibacterial activity for a coating may be determined by the ability of the coating on a coated textile to break up colonies of bacteria that may be deposited on a surface of the coated textile. In an embodiment, antibacterial activity for a coating may be determined by the ability of the coating on a coated textile to: (a) prevent the formation of a bacterial biofilm on the coated textile; and/or (b) reduce the size of a bacterial biofilm on the coated textile.

EXAMPLES

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to make and use the described embodiments, and are not intended to limit the scope of what the inventors regard as their disclosure nor are they intended to represent that the experiments below are all or the only experiments performed. Efforts have been made to ensure accuracy with respect to numbers used (*e.g.*, amounts, temperature, *etc.*) but some experimental errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, molecular weight is weight average molecular weight, temperature is in degrees Centigrade, and pressure is at or near atmospheric.

The compositions of this disclosure may be made by various methods known in the art. Such methods include those of the following examples, as well as the methods specifically exemplified below. As used herein in the working examples, “low molecular weight,” “low MW,” or “low-MW” silk fibroin fragments include fragments with a molecular weight between about 14 and about 30 kDa. As used herein in the working examples, “medium molecular weight,” “medium MW,” or “mid-MW” silk fibroin fragments include fragments with a molecular weight between about 39 and about 54 kDa.

Example 1: Tangential Flow Filtration (TFF) to Remove Solvent from Dissolved Silk Solutions

A variety of % silk concentrations have been produced through the use of Tangential Flow Filtration (TFF). In all cases a 1% silk solution was used as the input feed. A range of 750-18,000 mL of 1% silk solution was used as the starting volume. Solution is diafiltered in the TFF to remove lithium bromide. Once below a specified level of residual LiBr, solution undergoes ultrafiltration to increase the concentration through removal of water. See examples below.

7.30% Silk Solution: A 7.30% silk solution was produced beginning with 30 minute extraction batches of 100 g silk cocoons per batch. Extracted silk fibers were then dissolved using 100 °C 9.3 M LiBr in a 100 °C oven for 1 hour. 100 g of silk fibers were dissolved per batch to create 20% silk in LiBr. Dissolved silk in LiBr was then diluted to 1% silk and filtered through a 5 um filter to remove large debris. 15,500 mL of 1%, filtered silk solution was used as the starting volume/diafiltration volume for TFF. Once LiBr was removed, the solution was ultrafiltered to a volume around 1300 mL. 1262 mL of 7.30% silk was then collected. Water was added to the feed to help remove the remaining solution and 547 mL of 3.91% silk was then collected.

6.44% Silk Solution: A 6.44% silk solution was produced beginning with 60 minute extraction batches of a mix of 25, 33, 50, 75 and 100 g silk cocoons per batch. Extracted silk fibers were then dissolved using 100 °C 9.3 M LiBr in a 100 °C oven for 1 hour. 35, 42, 50 and 71 g per batch of silk fibers were dissolved to create 20% silk in LiBr and combined. Dissolved silk in LiBr was then diluted to 1% silk and filtered through a 5 um filter to remove large debris. 17,000 mL of 1%, filtered silk solution was used as the starting volume/diafiltration volume for TFF. Once LiBr was removed, the solution was ultrafiltered to a volume around 3000 mL. 1490 mL of 6.44% silk was then collected. Water was added to the feed to help remove the remaining solution and 1454 mL of 4.88% silk was then collected

2.70% Silk Solution: A 2.70% silk solution was produced beginning with 60 minute extraction batches of 25 g silk cocoons per batch. Extracted silk fibers were then dissolved using 100 °C 9.3 M LiBr in a 100 °C oven for 1 hour. 35.48 g of silk fibers were dissolved per batch to create 20% silk in LiBr. Dissolved silk in LiBr was then

diluted to 1% silk and filtered through a 5 um filter to remove large debris. 1000 mL of 1%, filtered silk solution was used as the starting volume/diafiltration volume for TFF. Once LiBr was removed, the solution was ultrafiltered to a volume around 300 mL. 312 mL of 2.7% silk was then collected.

Example 2: Silk fibroin chemically linked to Nylon

Synthesis of chemically modified silk fibroin: 6% Low silk: 100 mL, was reacted with 2,3-Dibromopropionyl chloride (7.2 g=0.028 mol), as shown in Fig. 1, to afford a silk-conjugate construct. Further application of this construct to a substrate including reactive groups, results in substrate coated with silk, wherein the silk is chemically linked to the substrate. As shown in Fig. 2, this disclosure is not limited to any particular linker, but rather discloses any suitable linker capable to chemically link silk to a substrate.

Example 3: Coating Substrates with a Silk-conjugate

Exhaustion: Nylon fabric: 300 g, LR: 1=13, temperature: 100 °C, time: 45 min, rinse, air dry. Nylon fabric (300g) is placed in a container with coating solution in a liquor ratio (LR) of 1:13. The container is closed, and the container is heated to 100 °C for 45 min. The container is cooled once the exhaustion process is completed. The fabric is rinsed with water, spinned to removed excess liquid, and allowed to air dry.

Samples used in various performance experiments:

Sample ID	Solution
STI-17100706	Control
STI-17100706-D001	Silk-Conjugate
STI-17100706-D002	Silk only
STI-17100706-D003	Precursor linker only

Comparative vertical wicking test results for nylon samples are shown in Figs. 4A and 4B (STI-17100706-D001: samples coated with silk-conjugate; STI-17100706-D002: samples coated with silk only; STI-17100706-D003: samples coated with precursor linker only; STI-17100706: control samples), at T=0 (Fig. 4A), and at T=3 (Fig. 4B). The higher the value the more water is absorbed by capillary action through the fabric, which results in better performing fabric. Samples coated with a silk-conjugate, and samples coated with silk only improve wicking compared to an unfinished control sample; samples coated with a silk-conjugate shows better wicking than samples coated with silk only;

unfinished control samples, and samples coated with a precursor linker only show almost no wicking.

Comparative absorbency test results for nylon samples coated with chemically modified silk fibroin are shown in Figs. 5A and 5B (STI-17100706-D001: samples coated with silk-conjugate; STI-17100706-D002: samples coated with silk only; STI-17100706-D003: samples coated with precursor linker only; STI-17100706: control samples), at T=0 (Fig. 5A), and at T=3 (Fig. 5B). Absorbency is measured in seconds. DNA: does not absorb the water drop, the test is stopped at 60 seconds. The lower the number, the faster the fabric absorbs, and therefore performance is better for moisture management. Samples coated with a silk-conjugate, and samples coated with silk only have a significantly improved absorbency, and samples coated with a silk-conjugate absorb better than samples coated with silk only; unfinished control samples and samples coated with the precursor linker only do not absorb at T=0.

Comparative dry rate test results for nylon samples coated with chemically modified silk fibroin are shown in Figs. 6A and 6B (STI-17100706-D001: coated with silk-conjugate; STI-17100706-D002: coated with silk only; STI-17100706-D003: coated with precursor linker only; STI-17100706: control), at T=0 (Fig. 6A), and at T=3 (Fig. 6B). Dry rate (mL/h) is how long the fabric takes to dry, a higher number means better performance. Samples coated with a silk-conjugate have an improved dry rate compared to the unfinished sample; samples coated with silk only have lower dry rate than unfinished control samples (Fig. 6A); at T=3 samples coated with a silk-conjugate show significant improvements (Fig. 6B).

Additional comparative vertical wicking test results for nylon samples are shown in Figs. 7A-7D (control: Fig. 7A; coated with silk only: Fig. 7B; coated with in-situ modified silk: Fig. 7C; coated with purified silk-conjugate: Fig. 7D), tested after a number (T) of laundering cycles (0, 3, and 20).

Additional comparative absorbency test results for nylon samples coated with chemically modified silk fibroin are shown in Figs. 8A-8D (control: Fig. 8A; coated with silk only: Fig. 8B; coated with in-situ modified silk: Fig. 8C; coated with purified silk-conjugate: Fig. 8D), tested after a number (T) of laundering cycles (0, 3, and 20).

Additional comparative dry rate test results for nylon samples coated with chemically modified silk fibroin are shown in Figs. 9A-9D (control: Fig. 9A; coated with silk only: Fig. 9B; coated with in-situ modified silk: Fig. 9C; coated with purified silk-conjugate: Fig. 9D), tested after a number (T) of laundering cycles (0, 3, and 20).

Comparative absorbency test results for nylon samples coated with silk fibroin chemically modified with natural crosslinkers are shown in Fig. 10 (control sample, sample coated with silk only, sample coated with silk modified with caffeic acid, sample coated with silk modified with genipin).

Example 4, Functionalized Silk

Functionalized Silk	Chemical Structure
(Low-MW-098-02-01)	
(Mid-MW-098-02-02)	
Hexamine (098-10-2)	
(Mid-MW-098-08-02)	

As used herein the symbols and conventions used in these processes, schemes and examples are consistent with those used in the contemporary scientific literature, for

example, the *Journal of the American Chemical Society* or the *Journal of Biological Chemistry*.

Unless otherwise indicated, all temperatures are expressed in °C (degrees Centigrade). All reactions conducted under an inert atmosphere at room temperature unless otherwise noted. Reagents employed without synthetic details are commercially available or made according to literature procedures.

HPLC/Mass spectra were obtained on Dyonex series 3000 HPLC coupled with Q Exactive™ Hybrid Quadrupole-Orbitrap™ Mass Spectrometer. Detection is by MS, UV at 214 nM using either Atmospheric Chemical Ionization (APCI) or Electrospray Ionization (ESI) and an evaporative light-scattering detector (ELSD). The data was acquired using Thermo Scientific™ Xcalibur™ Software. Data analysis was performed using PEAKS software.

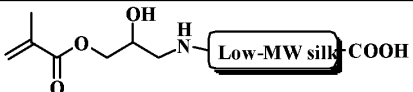
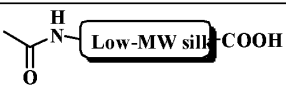
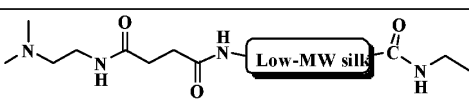
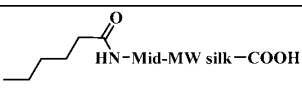
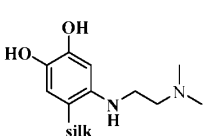
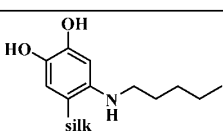
Silk fibroin is secreted in the form of a 2.3 MDa protein complex which consists of six sets of heavy chain-light chain heterodimer and one molecule of fibrohexamerin (P25). Covalent modification of silk fibroin was confirmed for different subunits (heavy chain, light chain, and/or fibrohexamerin) based on m/z and ms2 fragmentation patterns.

Prior to HPLC/MS, the functionalized silk synthesized was subjected to protease digestion according to the procedures below. In general, the functionalized silk in each sample were denatured with 6M guanidine HCl and reduced with DTT at 60 °C for 30 minutes followed by alkylation with iodoacetamide at room temperature in the dark. The alkylation reaction was quenched by the addition of excess DTT and the reaction was allowed to proceed for another 30 minutes at room temperature. Chymotrypsin digestion was carried out at 37 °C overnight at a protein to protease ratio of 1:50.

Attenuated Total Reflection was conducted on lyophilized functionalized silk samples using Nicolet iS50 FTIR Spectrometer.

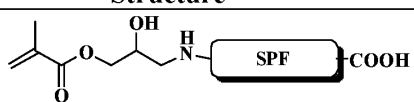
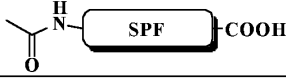
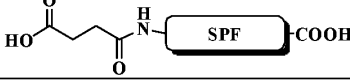
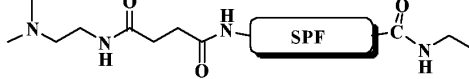
The functionalized silk prepared according to the experimental procedures described below are summarized below:

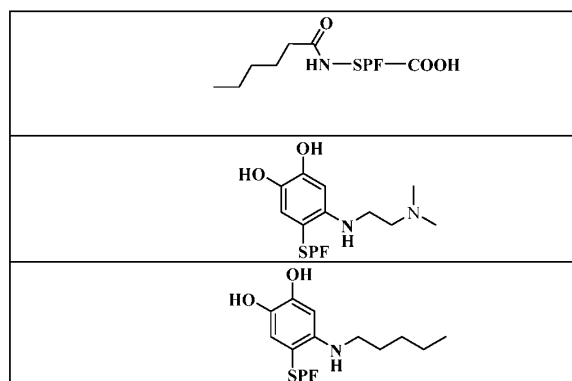
Sample ID	Structure	Characterization
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077-027-1		MS, IEF ^a
077-024-2		MS, IEF
077-028-2		MS, IEF
077-030-1		MS, IEF
098-08-02		FTIR
098-29-02		SEC-RI, FTIR
098-30-02		SEC-RI, FTIR

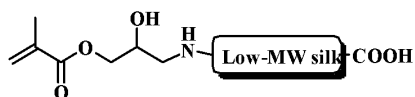
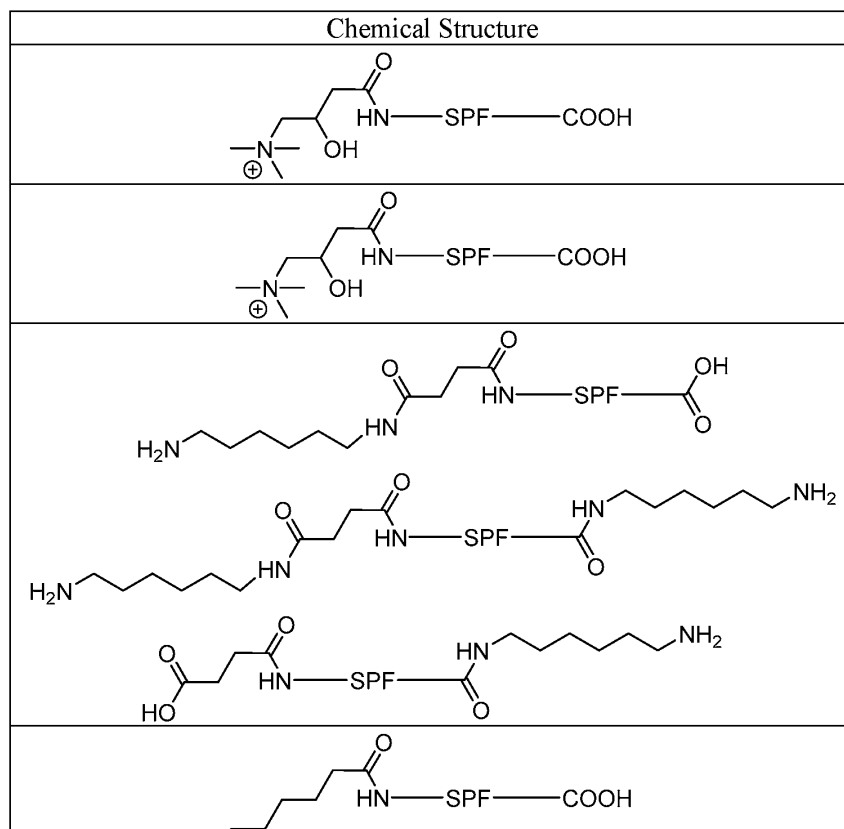
a. IEF stands for isoelectric focus.

Functionalized SPF:

Structure







Functionalized SPF:



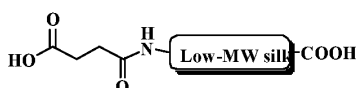
Low MW silk was placed on an ice bath and stirred at 300 rpm. The pH of the solution was adjusted to 9.5 and then glycidyl methacrylate was added in 3 portions, over 3 hours. After the addition, the ice bath was removed, and the mixture was allowed to warm up to room temperature (RT). The mixture was allowed to react at RT for 30 minutes. The reaction mixture was purified by dialysis against water using a 10 kDa MWCO dialysis tubing.

Covalent modification of Low-MW silk fibroin was confirmed for all three subunits (heavy chain, light chain, and fibrohexamerin) based on m/z and ms2 fragmentation patterns from the mass spectrum obtained in HPLC/MS analysis (See FIG. 9A and FIGs. 12A-B).



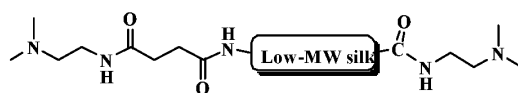
Low MW silk was placed on an ice bath and stirred at 300 rpm. Acetic anhydride was added in 3 portions, over 1 hour. After each portion the pH was adjusted to 8.5-9.5 with sodium hydroxide. After the last succinic acid addition, the ice bath was removed, and the reaction was allowed to warm up to room temperature. The mixture was allowed to react at RT for 30 minutes. The reaction mixture was purified by dialysis against water using a 10 kDa MWCO dialysis tubing.

Covalent modification of Low-MW silk fibroin was confirmed for all three subunits (heavy chain, light chain, and fibrohexamerin) based on m/z and ms2 fragmentation patterns from the mass spectrum obtained in HPLC/MS analysis (See FIG. 9B and FIGs. 13A-C).

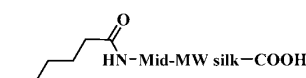


Low MW silk was placed on an ice bath and stirred at 300 rpm. Succinic anhydride was added in 3 portions, over 1 hour. After each portion the pH was adjusted to 8.5-9.5 with sodium hydroxide. After the last succinic acid addition, the ice bath was removed, and the reaction was allowed to warm up to room temperature. The mixture was allowed to react at RT for 30 minutes. The reaction mixture was purified by dialysis against water using a 10 kDa MWCO dialysis tubing.

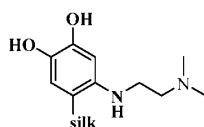
Covalent modification of Low-MW silk fibroin was confirmed for all three subunits (heavy chain, light chain, and fibrohexamerin) based on m/z and ms2 fragmentation patterns from the mass spectrum obtained in HPLC/MS analysis (See FIG. 9C and FIG. 14).



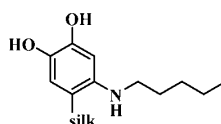
Covalent modification of Low-MW silk fibroin was confirmed for all three subunits (heavy chain, light chain, and fibrohexamerin) based on m/z and ms2 fragmentation patterns from the mass spectrum obtained in HPLC/MS analysis (See FIG. 9D and FIG. 15)



Mid MW silk was adjusted to pH 7.2 with phosphate buffer and heated to 37 °C. Hexanal was then added, followed by hydrogen peroxide and the solution was allowed to react with stirring 24 hr. The solution was then cooled to room temperature and purified by dialysis against water using a 10 kDa MWCO dialysis tubing.



Mid MW silk was adjusted to pH 6.5 in phosphate buffer and heated to 35 °C. Mushroom Tyrosinase was added and the solution was allowed to stir for 2 hr. The solution was then heated to 85 °C for 10 min to deactivate the tyrosinase enzyme, then the temperature was reduced to 60 °C and N,N-dimethylethylenediamine was added. The reaction mixture was allowed to react for 2 hr. The solution was then cooled to room temperature and purified by dialysis against water using a membrane with MWCO of 10 kDa.



Mid MW silk was adjusted to pH 6.5 in phosphate buffer and heated to 35 °C. Mushroom Tyrosinase was added and the solution was allowed to stir for 2 hr. The solution was then heated to 85 °C for 10 min to deactivate the tyrosinase enzyme, then the temperature was reduced to 60 °C and 1-aminopentane was added. The reaction mixture was allowed to react for 2 hr. The solution was then cooled to room temperature and purified by dialysis against water using a membrane with MWCO of 10 kDa.

The molecular weight bands of the functionalized silk samples was obtained by gel electrophoresis using Novex precast 3-10 IEF gels. The gel electrophoresis experiments were run according to ThermoFisher Novex “Pre-Cast Gel Electrophoresis Guide” Version B, January 27, 2003 IM-1002. In general, functionalized silk samples were diluted to 14.7 mg/ml protein concentration in 3-10 IEF sample buffer before loading and BioRad 4.45-9.6 IEF electrophoresis standards were used. The gels were focused at 100 constant volts for 1 hour, 200 constant volts for 1 hour, and 500 constant volts for 30 minutes. The gels were fixed in 12% TCA for ½ hour; stained in Coomassie Brilliant Blue R-250, stained in 10% acetic acid, and dried between cellophane sheets.

FIGs. 12A-B show the results for the electrophoresis gel experiments performed on the functionalized silk synthesized in Examples 10 above and the controls. FIG. 12A shows the electrophoresis gel from a few typical Activated Silks™, and FIG. 10B shows the electrophoresis gel for chemically modified Activated Silks™.

The mid-molecular weight Activated Silks™ have two isoelectric point ranges, one between pH 4-5 and a second one between pH 7-8. In contrast, low molecular weight Activated Silks™ have only one isoelectric point, in the range of pH 4-5. Upon chemical modification the isoelectric points of acetylated (sample 077-024-2) and methacrylated (sample 077-027-1) silks are unchanged. However, succinylation (sample 077-028-2) moves the isoelectric point to lower values (pH < 4.65), while amination (sample 077-030-1) move the isoelectric point to a higher value (pH 5.1-6) and give rise to an additional isoelectric point (pH 7-8).

Sample description for the gel electrophoresis samples shown in FIG. 10B

Lane	Sample	µg load	µl Load
1	BioRad IEF Stds	-	6

2	IEF Sample Buffer	-	7.35
3	077-024-2	100	7.35
4	077-027-1	100	7.35
5	077-027-2	100	7.35
6	077-028-2	100	7.35
7	077-030-1	100	7.35
8	MC-1	100	7.35
9	S700-SP	100	7.35
10	DBr-7	100	7.35
11	Ser-1	100	7.35
12	-	-	-

Molecular weight distribution for the functionalized silk samples was obtained by the size exclusion chromatography analysis. In general, sample solutions of the functionalized silk were analyzed on an Agilent 1100 HPLC equipped with a PolySep GFC P-4000 (7.8x300 mm) size exclusion column and a refractive index detector. The instrument was operated at a flow rate of 1 mL/min using a mobile phase containing 100 mM sodium chloride + 12.5 mM sodium phosphate buffer (pH 7), for a sample run time of 20 minutes. The molecular weight distribution was calculated relative to Dextran standards using the Cirrus software package.

FIG. 13 shows the chromatograms of two modified mid molecular weight silks compared to a typical mid molecular silk. The two modified silks have higher molecular weight compared to the standard (evidenced by the shift towards early elution times).

All patents, patent applications, and published references cited herein are hereby incorporated by reference in their entirety. While the methods of the present disclosure have been described in connection with the specific embodiments thereof, it will be understood that it is capable of further modification. Further, this application is intended to cover any variations, uses, or adaptations of the methods of the present disclosure, including such departures from the present disclosure as come within known or customary practice in the art to which the methods of the present disclosure pertain.

CLAIMS

1. An article comprising a coated substrate, wherein the coating comprises silk fibroin or silk fibroin fragments and a chemical modifier or a physical modifier.
2. The article of claim 1, wherein the chemical modifier is chemically linked to one or more of a silk fibroin side group and a silk fibroin terminal group.
3. The article of claim 2, wherein the silk fibroin side group and the silk fibroin terminal group are independently selected from an amine group, a carboxyl group, a hydroxyl group, a thiol group, and a sulfhydryl group.
4. The article of claim 1, wherein the chemical modifier is chemically linked to one or more functional groups on the substrate.
5. The article of claim 1, wherein the chemical modifier comprises one or more of a chemically linked functional group, or functional group residue, and a linker.
6. The article of claim 1, wherein the chemical modifier comprises one or more of $-\text{CR}^a_2-$, $-\text{CR}^a=\text{CR}^a-$, $-\text{C}\equiv\text{C}-$, $-\text{aryl}-$, $-\text{heteroaryl}-$, $-\text{O}-$, $-\text{S}-$, $-\text{OC}(\text{O})-$, $-\text{N}(\text{R}^a)-$, $-\text{N}=\text{N}-$, $=\text{N}-$, $-\text{C}(\text{O})-$, $-\text{C}(\text{O})\text{O}-$, $-\text{OC}(\text{O})\text{N}(\text{R}^a)-$, $-\text{C}(\text{O})\text{N}(\text{R}^a)-$, $-\text{N}(\text{R}^a)\text{C}(\text{O})\text{O}-$, $-\text{N}(\text{R}^a)\text{C}(\text{O})-$, $-\text{N}(\text{R}^a)\text{C}(\text{O})\text{N}(\text{R}^a)-$, $-\text{N}(\text{R}^a)\text{C}(\text{NR}^a)\text{N}(\text{R}^a)-$, $-\text{N}(\text{R}^a)\text{S}(\text{O})_t-$, $-\text{S}(\text{O})_t\text{O}-$, $-\text{S}(\text{O})_t\text{N}(\text{R}^a)-$, $-\text{S}(\text{O})_t\text{N}(\text{R}^a)\text{C}(\text{O})-$, $-\text{OP}(\text{O})(\text{OR}^a)\text{O}-$, wherein t is 1 or 2, and wherein at each independent occurrence R^a is selected from hydrogen, alkyl, alkenyl, fluoroalkyl, carbocyclyl, carbocyclalkyl, aryl, aralkyl, heterocycloalkyl, heterocycloalkylalkyl, heteroaryl, or heteroarylalkyl.
7. The article of claim 1, wherein the coating comprises one or more of low molecular weight silk fibroin or silk fibroin fragments, medium molecular weight silk fibroin or silk fibroin fragments and high molecular weight silk fibroin or silk fibroin fragments.

8. The article of claim 1, wherein the coating comprises silk fibroin or silk fibroin fragments with an average weight average molecular weight from about 5 kDa to about 144 kDa.

9. The article of claim 1, wherein the coating comprises silk fibroin or silk fibroin fragments with an average weight average molecular weight from about 1 kDa to about 5 kDa, from about 5 kDa to about 10 kDa, from about 6 kDa to about 17 kDa, from about 10 kDa to about 15 kDa, from about 15 kDa to about 20 kDa, from about 17 kDa to about 39 kDa, from about 20 kDa to about 25 kDa, from about 25 kDa to about 30 kDa, from about 30 kDa to about 35 kDa, from about 35 kDa to about 40 kDa, from about 39 kDa to about 80 kDa, from about 40 kDa to about 45 kDa, from about 45 kDa to about 50 kDa, from about 60 kDa to about 100 kDa, or from about 80 kDa to about 144 kDa.

10. The article of claim 1, wherein the coating comprises silk fibroin or silk fibroin fragments with a polydispersity between 1 and about 5.0.

11. The article of claim 1, wherein the coating comprises silk fibroin or silk fibroin fragments which prior to coating the substrate are stable in a solution.

12. The article of claim 1, wherein the coating comprises silk fibroin or silk fibroin fragments which prior to coating the substrate do not spontaneously or gradually gelate and do not visibly change in color or turbidity when in a solution for at least 10 days.

13. The article of claim 1, wherein the substrate includes one or more of a fiber, a thread, a yarn, a fabric, a textile, a cloth, or a hide.

14. The article of claim 13, wherein the fabric, textile, or cloth is woven or nonwoven.

15. The article of claim 13, wherein the fiber, thread, or yarn comprises one or more of polyester, recycled polyester, Mylar, cotton, nylon, recycled nylon, polyester-polyurethane copolymer, rayon, acetate, aramid (aromatic polyamide), acrylic, ingeo (polylactide), lurex (polyamide-polyester), olefin (polyethylene-polypropylene), and combinations thereof.

16. The article of claim 13, wherein the fiber, thread, or yarn comprises one or more of alpaca fiber, alpaca fleece, alpaca wool, lama fiber, lama fleece, lama wool, cotton, cashmere, sheep fiber, sheep fleece, sheep wool, byssus, chiengora, qiviut, yak, rabbit, lambswool, mohair wool, camel hair, angora wool, silkworm silk, abaca fiber, coir fiber, flax fiber, jute fiber, kapok fiber, kenaf fiber, raffia fiber, bamboo fiber, hemp, modal fiber, pina, ramie, sisal, and soy protein fiber.

17. The article of claim 13, wherein the fiber, thread, or yarn comprises one or more of mineral wool, mineral cotton, man-made mineral fiber, fiberglass, glass, glasswool, stone wool, rock wool, slagwool, glass filaments, asbestos fibers, and ceramic fibers.

18. A method of coating a substrate with a coating comprising silk fibroin or silk fibroin fragments and a chemical modifier or a physical modifier, the method comprising applying to the substrate at least one composition comprising silk fibroin or silk fibroin fragments with an average weight average molecular weight from about 1 kDa to about 144 kDa, and a polydispersity between 1 and about 5.0.

19. The method of claim 18, further comprising applying to the substrate a chemical modifier or a physical modifier selected from a wetting agent, a detergent, a sequestering or dispersing agent, an enzyme, a bleaching agent, an antifoaming agent, an anti-creasing agent, a dye dispersing agent, a dye leveling agent, a dye fixing agent, a dye special resin agent, a dye anti-reducing agent, a pigment dye system anti-migrating agent, a pigment dye system binder, a delave agent, a wrinkle free treatment, a softener, a handle modifier, a waterborne polyurethane dispersion, a finishing resin, an oil or water

repellant, a flame retardant, a crosslinker, an activator, a thickener for technical finishing, or any combination thereof.

20. The method of claim 19, wherein the crosslinker or the activator are independently selected from a N-hydroxysuccinimide ester crosslinker, an imidoester crosslinker, a sulfosuccinimidyl aminobenzoate, a methacrylate, a silane, a silicate, an alkyne compound, an azide compound, an aldehyde, a carbodiimide crosslinker, a dicyclohexyl carbodiimide activator, a dicyclohexyl carbodiimide crosslinker, a maleimide crosslinker, a haloacetyl crosslinker, a pyridyl disulfide crosslinker, a hydrazide crosslinker, an alkoxyamine crosslinker, a reductive amination crosslinker, an aryl azide crosslinker, a diazine crosslinker, an azide-phosphine crosslinker, a transferase crosslinker, a hydrolase crosslinker, a transglutaminase crosslinker, a peptidase crosslinker, an oxidoreductase crosslinker, a tyrosinase crosslinker, a laccase crosslinker, a peroxidase crosslinker, a lysyl oxidase crosslinker, and combinations thereof.

21. The method of claim 18, wherein the composition comprises low molecular weight silk fibroin or silk fibroin fragments.

22. The method of claim 18, wherein the composition comprises medium molecular weight silk fibroin or silk fibroin fragments.

23. The method of claim 18, wherein the composition comprises high molecular weight silk fibroin or silk fibroin fragments.

24. The method of claim 18, wherein the composition comprises a chemical fabric softener.

25. The method of claim 18, wherein the composition comprises a Brønsted acid.

26. The method of claim 18, further comprising dyeing the substrate prior to applying to the substrate the at least one composition comprising silk fibroin or silk fibroin fragments.

27. The method of claim 18, further comprising dyeing the substrate after applying to the substrate the at least one composition comprising silk fibroin or silk fibroin fragments.