

**FIBERS COMPRISING PROTEIN AND POLYMER COMPONENTS, METHODS OF
USE, METHODS OF MANUFACTURE, AND RELATED THREADS, YARNS,
TEXTILES, AND FABRICS THEREOF**

[001] This application claims priority to U.S. Provisional Patent Application Ser. No. 63/619,265, filed on January 9, 2024, the disclosure of which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[002] This application relates to compositions of matter manufactured from proteins and containing high or low molar mass additives to aid processability, and more specifically protein or additive modified protein materials suitable for melt-spinning into fiber. It also relates to methods of manufacturing structural protein-synthetic polymer materials, utilization thereof, and products composed thereof—including, but not limited to, textiles.

BACKGROUND

[003] Proteins are bioderived, biodegradable molecules that have evolved to serve specific biological functions. Natural forms of certain proteins, for example, keratin (*e.g.*, in wool and other animal hair), and silk (*e.g.*, in cocoons of various arthropods such as silk worms), have an excellent balance of utility and aesthetic properties, for example mechanical strength, low-thermal conductivity, and attractive appearance, that has for eons made them attractive materials for textiles and other goods.

[004] Polyester and other synthetic polymers are relatively cheap and easy to manufacture, and are commonly used in textiles, bottles, and other manufactured products. Such synthetic polymers may be characterized as consisting of simple repeating chemistry; they may vary in molecular length, often with little or no change in their observable characteristics. Unlike proteins—which are biological polymers imbued with function as a result of their complex bio-chemical folding (assuming they are not denatured)—synthetic polymers typically fold and interpenetrate in a substantially random structure. Likely as a result of such chemistry, it has proven difficult or impossible to generate textiles from synthetic polymer fibers that substantially mimic beneficial characteristics of protein-fiber-based textiles—especially in an economic fashion.

[005] While naturally-occurring protein fibers may be harvested from biological sources and processed to obtain silk thread, wool yarn, and the like for assembly into textiles via, for example, weaving or knitting, obtaining such protein-based fibers is relatively expensive and labor

intensive—especially when compared to manufacturing synthetic polymer fibers through modern industrial techniques and/or harvesting plant-based (typically carbohydrate) fibers (e.g., cotton and bamboo). That is, procurement of cashmere, other wools, raw silk, and the like requires substantial agricultural activity before the manufacturing processes can even begin. Indeed, throughout human history and to date, protein-based fibers (silk, cashmere, wool, etc.) utilized in textiles have all been generated biologically. At the same time, waste proteins are readily available at low cost: For example, the poultry industry generates copious amounts of chicken feathers—which substantially comprise keratin—as a waste product.

[006] Cost effective use of such waste proteins is limited by the difficulty of reprocessing proteins into new useful items; such attempts usually involving costly solution procedures that tend to cause the attractive attributes of these proteins to be lost. Structural proteins like keratin and silk are generally understood to be partially crystalline and may denature and/or decompose at temperatures lower than their melting temperatures, making low cost thermal processing (e.g., melt processing) of such protein waste into new useful textile products previously unattainable.

[007] Scientists have attempted to combine proteins and plastics to arrive at new and useful materials. For example, with reference to US Patent Nos. 9,706,789 and 10,595,546, inventor Walter Schmidt previously pioneered processes of plasticizing waste proteins (e.g., keratin and silk) via various nitrogen-containing compounds to arrive at melt-stable protein compositions for use in animal feed and solid industrial products like flower pots. Notably, however, such processes and patents did not contemplate the generation of fibers or other materials suitable for textile manufacturing. As another example, with reference to U.S. Patent No. 5,705,030, Schmidt and other scientists devised methods to generate fibers and fiber pulp from waste chicken feathers. But, the claimed resulting compositions neither meaningfully incorporated synthetic polymers nor could be readily processed via existing synthetic polymer processing equipment to produce thread or textiles.

[008] Accordingly, processes for economically manufacturing fibers, thread, and textiles with characteristics of (or approaching) naturally-derived cashmere, other wools, silk, and/or the like—as well as resulting textiles and other products—are desired by the market. It would be advantageous if such techniques could substantially utilize existing, widespread manufacturing equipment currently utilized to melt process synthetic polymers into fibers, yarns, and textiles. It would be further advantageous if such techniques could utilize waste protein material, for example,

chicken feathers, that can be obtained at minimal cost and/or may benefit the environment via utilization of an industrial waste product. Additionally, it would be advantageous if such resulting fibers and textiles consist of or substantially comprise renewable, sustainable, and/or biodegradable materials; this may serve to beneficially lower the impact of fiber processing on energy resources and CO₂ generation.

SUMMARY

[009] The technology disclosed herein advantageously provides processes for manufacturing of fibers—and corresponding yarns and textiles—that possess both noble fiber aesthetics (e.g., cashmere, Marino, silk) with synthetic fiber processibility and cost-performance.

[010] The present disclosure provides a description of exemplary protein-high or low molar mass compositions to address the perceived problems described above, as well as methods of manufacture, methods of use, and related products and components thereof. It is to be understood that the descriptions herein are exemplary and explanatory only and are not restrictive of the inventive concepts disclosed.

[011] In exemplary embodiments, the disclosed technology allows proteins, especially structural proteins to utilize well-known, low-cost melt processing technologies (e.g., fiber spinning, film extrusion, injection molding) to produce new families of products that retain the essential bio-derived properties of proteins. As discussed herein, such technology may utilize additives to permit low-cost, stable melt processing of structural proteins into new products, for example textile fibers, that may fully or substantially retain the aesthetic properties of the starting protein. In certain embodiments, biodegradability may be preserved by substantially only utilizing additives that are themselves biodegradable, such as, but not limited to, low molar mass amino acids, low molar mass aliphatic hydroxy acids, high molar mass aliphatic polyesters, high molar mass oligopeptides and/or the like.

[012] In one exemplary embodiment, a yarn comprising a plurality of fibers is provided. Each fiber may include at least 0.5% protein by weight and a synthetic polymer.

[013] Each of the plurality of fibers may be a melt-spun fiber.

[014] For each of the plurality of fibers, an outer portion may have a higher density of protein particles than an inner portion.

[015] Each fiber may be a skin-core fiber comprising an inner core and an outer sheath. The outer sheath of each of fiber may include at least 1% protein by weight. The inner core of each fiber may include less than 1% and/or less than 0.1% protein by weight.

[016] Each outer sheath may comprise at least 35% of its respective skin-core fiber by weight.

[017] The protein may be keratin or silk. The synthetic polymer may have a melting point of less than 250°C.

[018] Each of the plurality of fibers may have a diameter of between 8 and 20 microns. An outer surface of each outer sheath includes a plurality of circumferential surface cracks. The plurality of circumferential surface cracks may be spaced apart by between 0.5 and 2 microns.

[019] The yarn may be a filament yarn.

[020] The yarn may be a staple yarn. Each fiber may have a diameter of between 8 and 20 microns. Each fiber may have a length of between 20 and 128 mm. An outer surface of each outer sheath may a plurality of circumferential surface cracks. The plurality of circumferential surface cracks may be spaced apart by between 0.5 and 2 microns.

[021] Each of the plurality of fibers may be crimped. Each fiber may have between 5 and 20 crimps per inch and/or between 9 and 15 crimps per inch.

[022] In another embodiment, fabric woven from a yarn comprising a plurality of fibers is provided. Each fiber may include at least 0.5% protein by weight and a synthetic polymer. The fabric may have no or negligible discernable scroop to a human ear, similar to fabrics made from cashmere and unlike typical synthetic polymer fabrics.

[023] In various other embodiments, methods of manufacture of fibers, yarns, and textiles are provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[024] The accompanying drawings, which are incorporated into and constitute a part of this specification, illustrate several embodiments and aspects of the apparatuses and methods described herein and, together with the description, serve to explain the principles of the invention.

[025] FIGS. 1 is a high-level flow chart describing a method of manufacturing textiles from protein and synthetic polymers, in accordance with exemplary embodiments.

[026] FIG. 2 is an illustration of one measure of aesthetic properties in fibers and textiles, namely thermal effusivity.

[027] FIG. 3 is an illustration of a melt-spinning technique for generating filament yarn, in accordance with exemplary embodiments.

[028] FIG. 4 is a photo of melt-spun protein-synthetic polymer filament yarn wrapped on a bobbin after melt-spinning, in accordance with exemplary embodiments.

[029] FIGS. 5A, 5B, and 5C are scanning electron microscope (SEM) images of melt-spun protein-synthetic polymer staple yarn fibers at 250X, 500X, and 2500X magnification, respectively, in accordance with exemplary embodiments.

[030] FIGS. 6A, 6B, and 6C are scanning electron microscope (SEM) images of melt-spun protein-synthetic polymer filament yarn fibers at 200X, 500X, and 2500X magnification, respectively, in accordance with exemplary embodiments.

[031] FIGS. 7A and 7B are Confocal Raman Microscopy images of a melt-spun protein-synthetic polymer filament and staple fibers, respectively, in accordance with exemplary embodiments.

[032] FIGS. 8A, 8B, and 8C are Energy-Dispersive X-ray spectroscopy (EDX) images depicting Nitrogen (N) signatures of melt-spun protein-synthetic polymer filament yarn fibers, melt-spun protein-synthetic polymer staple yarn fibers, and keratin protein, respectively, in accordance with exemplary embodiments.

[033] FIGS. 8D, 8E, and 8F are Energy-Dispersive X-ray spectroscopy (EDX) images depicting Sulfur (S) signatures of melt-spun protein-synthetic polymer filament yarn fibers, melt-spun protein-synthetic polymer staple yarn fibers, and keratin protein, respectively, in accordance with exemplary embodiments.

[034] FIGS. 9A, 9B, and 9C are Fourier Transform Infrared Spectroscopy (FTIR) results for keratin, PLA, and compounded batch of keratin-PLA, respectively, in accordance with exemplary embodiments.

DETAILED DESCRIPTION

[035] With reference to FIG. 1, an exemplary method 100 of manufacturing textiles utilizing protein and synthetic polymer is disclosed. In exemplary embodiments, method 100 may be directed to generation and utilization of melt-spun protein-synthetic polymer filament yarn and/or staple yarn.

[036] As in step 110, suitable protein may be sourced, preferably from agricultural waste and/or via recycling of discarded protein-based textiles, other materials, and/or components thereof.

[037] In exemplary embodiments, the protein utilized may comprise, consist of, or substantially consist keratin, but this disclosure is not so limited. Keratin is the protein that defines the chemistry of attractive naturally-occurring fibers like wool, cashmere, marino wool, alpaca, angora, camel, mohair, and/or the like. It is also the protein of other animal hair, human hair, feathers, nails, hooves, and/or the like. The inventors have determined that utilization of keratin in method 100 may result in economical fiber/textile production and resulting textiles with superior aesthetic qualities that approximate those of textiles made from naturally-occurring keratin fibers.

[038] Poultry feathers, *e.g.*, the feathers of birds raised as food, are a generally regarded as a waste product and are typically either ground to provide a component of animal feed or buried in landfills. Billions of pounds of poultry feathers, and more specifically chicken feathers, are discarded annually and are contemplated as a preferred suitable protein source. However, this disclosure is not so limited: duck, turkey, and other bird feathers may be used. In various embodiments, feathers from the head, wings, and or feet of birds may be utilized or omitted. The keratin source may comprise intact feathers, broken feathers, and/or feather fluff. However, based on current experimentation and research by the inventors, it appears that utilization of feather rachis and barbs is unlikely to result in fibers with meaningfully different characteristics than utilization of only fluff.

[039] Additionally, it is contemplated that poultry feathers may be selected in whole or in part based on feather color that may ultimately be imparted (at least in part) into resulting protein-synthetic polymer compositions, as well fibers thereof and yarns and textiles incorporating the same.

[040] In alternative embodiments, it is contemplated that other keratin-containing animal products and byproducts may be utilized as a protein source. For example, the protein source may comprise waste wool; cashmere waste; hair (including, but not limited to, discarded human and pet hair); animal horns, nails, and claws; and/or other keratin sources.

[041] This disclosure, however, is not limited to utilization of keratin and keratin-containing materials as a protein source. In alternative embodiments, silk and/or other suitable animal proteins, and/or other structural proteins, such as those derived from soy, may be utilized.

[042] After the protein source is procured, the process may proceed to step 130.

[043] As in step 130, the protein may be synthesized and/or prepared for plasticization. This may include sub-steps of washing and drying the raw protein source, reducing the size of the

protein source material, grinding the protein source material to a desired particle size or particle size range, and/or drying the powdered protein.

[044] For example, preparing keratin from waste poultry feathers may include washing the feathers and coarsely chopping the feathers for further processing (assuming, for example, chopped feathers and/or feather fluff is not provided as the protein source). The cleaned, chopped feathers may then be ground to a powder with substantially uniform particle size, for example of <100 micron. However, in some embodiments mean particle size of less than 10 microns, for example, between 5 and 7 microns, and/or with an aspect ratio less than 40 may be used. The ground feather powder may then be further dried, for example to <100 ppm water.

[045] In another example, waste wool or cashmere may be washed, chopped, ground, and/or dried to arrive at a suitable processed protein powder.

[046] Removing substantial water content may be particularly important or desirable where the protein powder is to be compounded with a polyester carrier, such as PHA, PEF, PLA, PP and/or PET, in step 150. This is because bio-based and similar synthetic polymers are hydrolytically unstable; the retention of excessive moisture in the protein powder is likely to undermine creation of resulting fibers and textiles, and/or may at least negatively affect their characteristics.

[047] It may be noted that, at the conclusion of step 130, the resulting protein powder is unlikely to consist entirely of the desired protein, e.g., keratin. That is, smaller amounts of other proteins, carbohydrates, other animal byproduct, and/or miscellaneous substances are contemplated to remain in the powder. The inclusion of limited amounts of such impurities (e.g., less than 5%, less than 1%, less than 0.5%, less than 0.1 %, and/or less than 0.01%) in the prepared protein powder is unlikely to substantially undermine the remaining steps of method 100 or the characteristics of resulting fibers or textiles.

[048] The process may proceed to step 150.

[049] As in step 150, the protein may be plasticized and rendered melt-stable via combination with a carrier molecule. In exemplary embodiments, such step may occur via melt extrusion, for example, on existing industrial scale melt extruders. As part of or prior to step 150, an appropriate carrier (and/or additives) may be selected and the desired protein to carrier ratio may be determined.

[050] Important characteristics for polymer carrier selection may include (1) a polymer melt temperature that is lower than the degradation temperature of the selected protein (e.g., 250°C for

keratin), and (2) a compounding compatibility between the protein and carrier. As to (2), it may be noted that the compatibility is not expected to require integration on a molecular level—but rather that the carrier polymer can suitably bind to and thereby link to the protein molecules.

[051] Suitable additives may include nitrogen containing molecules and/or hydroxyl containing molecules. In certain exemplary embodiments, the carrier-additives may comprise low molar mass molecules—for example, amino acids, aliphatic hydroxy acids, and/or the like—and/or high molar mass molecules—for example, oligopeptides of aliphatic polyesters, and/or the like.

[052] In certain exemplary embodiments, PLA, other polylactides, polyhydroxyalkanoates other polyesters, and/or other synthetic polymers with a melting temperature less than 250°C may be utilized as a carrier. In this manner, keratin (or other proteins) may intimately mixed with biopolymers such as PHA, PEF, PLA and/or PET, and/or other high molar mass carrier during the compounding process. In turn, hot melt processing at lower temperatures may substantially prevent or at least reduce the incidence of degrading of keratin or other processed protein. Of note, the art suggests that biopolymers such as PHA, PEF, and/or PLA may improve the thermal stability of keratin and/or other proteins, thereby enabling compounding and hot melt spinning at higher temperatures.

[053] In certain exemplary embodiments, the carrier may comprise polylactide. Advantageously polylactide is a degradable synthetic polyester that may be obtained entirely from renewable resources. In other exemplary embodiments, the carrier polymer may comprise PET, polyolefins, biopolyolefins, biopolypropylene, maleated biopolypropylene, bionylons, and/or the like. In some embodiments, it may be necessary for the selected carrier to fully or at least partially crystallize to achieve desirable mechanical properties and thermal stability in the resulting fiber. It may be noted, however, that PET may have an undesirably high melting point.

[054] As to the ratio of prepared powdered protein (including limited inclusions of other proteins and byproduct components, as discussed above) to synthetic polymer carrier or low molar mass modifier, a wide range is contemplated. For example, keratin concentration in desirable fiber compositions may range from around 1% to greater than 90% by weight, or as low as 0.5% in alternative embodiments. The inventors have confirmed that the addition of even low concentrations of keratin to polymeric additives imparts aesthetic characteristics associated with biologically produced keratin fibers while retaining the flexibility of synthetic polymer melt spinning and fiber manipulation technologies to create new, desirable textile products. It is

contemplated, however, that different protein-carrier ratios are likely to impart distinct characteristics in the produced fibers and textiles. For example, the inventors' research and experimentation suggests that higher percentage of keratin content are likely to impart aesthetic textile characteristics akin to silk.

[055] Once the polymer carrier is selected and appropriate amounts of protein powder and carrier are provided, they may be compounded together. In certain preferred embodiments, compounding may be improved by first grinding the protein powder to a uniform and small particle size. In some embodiments, mean particle sizes equal to or less than the diameter of the starting keratinous material may be preferred. For example, such mean particle sizes may be less than about 10 micron, between 5 and 8 microns (for example, at or around 6 or 7 microns), and/or less than 5 microns in various embodiments.

[056] In certain exemplary embodiments, the composition components may be compounded via a twin screw extruder. Prior to such extrusion, drying or redrying the carrier polymer to <100 PPM water—especially if it comprises PLA and/or PHA—may be desired to maximize stability during processing. It is contemplated that the extrusion screws should be designed for moderate to intensive mixing and high shear. The inventors have determined that while too little dispersion and shear will insufficiently combine the protein and carrier, too much shear may alter the molecular weight of the polymer carrier and/or lead to degradation of the protein component. During the extrusion process, time and temperature of processing should be controlled to minimize or eliminate protein decomposition and/or denaturing.

[057] In exemplary embodiments, the twin screw extruder may preferably provide the protein-polymer composition in the form of rods. The extruded protein-polymer composition may preferably be pelletized for storage, transport, and/or sale—and for further processing in accordance with typical polymer/polymer fiber manufacturing techniques. In some embodiments, the rods and/or pellets may be cooled via water bath or similar. If such sub-step is employed, re-drying the pellets (or rods) may be advisable to minimize potential hydrolytic instability.

[058] As would be appreciated by a person of skill in the art, the extruded protein-synthetic polymer composition may have a higher concentration of protein and/or additives than may ultimately be utilized in fiber formation (*e.g.*, step 170 below).

[059] The process may proceed to step 170. It is contemplated, however, that in certain embodiments, the polymer composition may be transported and/or sold such that step 170 may

occur at a different location (e.g., a melt-spinning facility) and/or may be effectuated by a different entity.

[060] As in step 170, the extruded polymer may be formed into fiber via melt spinning. Advantageously, existing melt-spinning technologies may be used to manufacture the fiber at scale. With reference to Fig. 3, a conventional process for melt-spinning on a continuous process machine is shown.

[061] In exemplary embodiments, melt-spinning may proceed on commercially available equipment that is compatible with the utilized carrier-polymer and at temperatures suitable for melt-spinning such carrier-polymer, but preferably at the low end of such range. As with the step 150, during melt-spinning process 170, time and temperature of processing should to be controlled to minimize or eliminate protein decomposition and/or denaturing. Preferably, the melt-spinning may be characterized by uniform quench.

[062] The total fiber draw down in spinning and draw ratio in the solid state may be set to obtain a desired fiber diameter. It is expected that certain fiber characteristics may be manipulated by the total fiber draw ratio. For example, thicker fibers may improve strength or durability and thinner fibers may correspond to a softer feel. Various desired fiber diameters and their associated characteristics may be experimentally determined, with conventional synthetic polymer fiber diameters and known animal fiber diameters (*see, e.g., https://en.wikipedia.org/wiki/Animal_fiber*) used as starting points. The inventors believe that, in exemplary embodiments, melt-spun polymer fiber diameters and/or lengths may be selected to approximate fiber diameters and/or lengths of a natural fiber for which textile characteristics are desired. For example, where silk-like characteristics are desired melt-spun polymer fiber diameters and/or lengths should match or approximate those of silk, about 10 microns; such fibers may also spun drawn using multi-lobal or triangular-shaped (e.g., equilateral triangles) spinnerets. For example, triangular-shaped fibers may correspond to increased sheen in a resulting fabric. In various embodiments, fibers may be drawn to have a diameter of between 8 and 20 microns or more narrowly between 12 and 18 microns, or between 11 and 13 microns.

[063] In certain embodiments, skin-core melt spinning technology may be employed to create filaments with higher keratin concentration in the skin to maximize beneficial characteristics. For example, in some embodiments, substantially all of the protein in the fiber may be present in the filament sheath--with the filament core free or substantially free of protein. For example, in various

embodiments, the core may comprise less than 1%, less than 0.1%, less than 0.01%, negligible, and/or no measurable amount of protein by weight. In various embodiments, the sheath may comprise more than 0.5%, more than 1%, more than 2%, more than 5%, or more than 10% protein by weight. The sheath may comprise less than 20%, less than 40%, less than 50%, less than 75%, and/or less than 90% protein by weight. However, it is believed that certain properties may degrade with sheath protein content of greater than 40%. It is contemplated that provision of all, substantially all, or most protein within the sheath is likely to maximize improved aesthetic fiber properties while minimizing potential reduction in fiber strength. In certain skin-core fiber embodiments, additives may be provided to form the sheath to improve dyeability of the fibers and/or protein particles therein. In various preferred skin-core fiber embodiments, the sheath may comprise at least 35%, 40%, 45%, or 50% of the resulting fibers.

[064] The process may proceed to step 175. It is contemplated, however, that in certain embodiments, the spun filaments may be transported and/or sold such that subsequent steps may occur at a different location (e.g., a textile factory) and/or may be effectuated by a different entity.

[065] As in step 175, the filaments may be treated. With reference to, for example, melt spin fiber example 1, below, this step may be omitted in certain embodiments.

[066] With reference to, for example, melt spin fiber examples #2 and #3 (discussed below), the spun fibers may undergo controlled surface crazing. As would be appreciated by a person of ordinary skill in the art, even in non-surface crazing embodiments, fibers may be drawn in their solid state at a specified draw ratio, for example between 2.5 and 3.5. Controlled surface crazing may use a draw ratio approximately 20% to 30% higher, or about 25%, than what might be conventionally used in the art for like fibers. For example, each solid state fiber may be drawn longer via a higher draw ratio, for example, at draw ratios of 3.8 to 4, 4 to 4.2, or 4.2 to 4.4 to create microcracks on its outermost surface. Such microcracks inherently generate microvoids, increasing surface area of such fibers, which may expose additional protein particles and thereby improve aesthetic properties. With reference to FIG. 6C, microcracks on a fiber's external surface may be generally circumferential and may be spaced at between 0.5 and 2 microns, for example around 1 micron.

[067] The inventors believe that such surface crack morphology may cause the fibers (and corresponding yarns and textiles) to appear lighter due to light scattering, improve aesthetic feel and drape of corresponding textiles, enhance the process of dyeing the resulting yarns and fabrics,

and/or the like. A person of ordinary skill in the art would find these advantages to surface crack morphology to be unexpected because, for PHA, PLA, and other synthetic polymer fibers, surface cracking is generally understood to be undesirable for textile because, for example, it may reduce tensile strength. Based on experimental data, fiber embodiments disclosed herein are expected to have tensile strength of 3.5-5 g/ denier, or more narrowly 3.75-4.5 g/ denier—substantially exceeding that of wool and similar to that of uncracked PLA fibers.

[068] In staple yarn embodiments, with reference to, for example, melt spin fiber example #4 (discussed below), the melt-spun fibers may be crimped and heat-treated before being cut and utilized in yarn formation (e.g., step 180 below). It is contemplated that cut lengths and crimp frequency may be selected to mimic characteristics of noble or other animal hair fibers sought to be emulated. Known crimping technology, including thermal crimping technology, may be utilized on staple fiber (and/or filament fibers), including, for example, by heat treating the crimped fibers at a temperature exceeding expected dye bath temperatures. In various embodiments, fibers may be subject to “soft” or “hard” crimping at various depths, may be crimped at between 5 and 20 crimps per inch (CPI), and/or more narrowly between 9 and 15 CPI. In certain preferred embodiments “soft” crimps may obtain superior aesthetic qualities, including perceived softness of a resulting fabric: For example, 6-8 CPI may mimic certain aesthetic characteristics of Cashmere and 9-11 CPI may mimic certain aesthetic characteristics of Marino wool. In various embodiments, cut lengths may be between 20 and 128 mm or more narrowly between 35 and 60 mm.

[069] Additionally or alternatively, false twist texturing may be used to add bulk. These and other embodiments may employ cutting fibers into short lengths like natural wool or cashmere; creating staple fibers that can be twisted (spun) into yarn; texturing the product, filament, or staple, to create bulk similar to natural fibers; and/or the like.

[070] In certain alternative embodiments, fibers may be shaped (or spun) to have a non-circular cross sections, for example, triangular or multi-lobal, and thereby further comport with the cross-sectional morphology of naturally-occurring silk or other fibers.

[071] The process may proceed to step 180. It is further contemplated, however, that in certain embodiments, the spun (and/or treated) fiber may be transported and/or sold such that subsequent steps may occur at a different location (e.g., a textile factory) and/or may be effectuated by a different entity. It is also contemplated that, in some embodiments, steps 180 and 185 may be omitted if, for example, textile manufacturing (step 190) utilizes monofilaments rather than yarns.

[072] As in step 180, treated filaments and/or unprocessed filaments (if step 175 is omitted) may be processed into staple and/or filament yarn using, for example, methods known in the art.

[073] The process may proceed to step 185. It is further contemplated, however, that in certain embodiments, the yarn may be transported and/or sold such that subsequent steps may occur at a different location (e.g., a textile factory) and/or may be effectuated by a different entity. It is also contemplated that, in some embodiments, step 185 may be omitted entirely in some embodiments.

[074] As in step 185, the yarn may be treated by dyeing, and/or other methods known in the art. As a person of ordinary skill in the art would understand, fibers and yarns disclosed herein are expected to inherently accept virtually all dye chemistries effective on utilized proteins due to their inclusion of such protein components. Such susceptibility to conventional dyeing may also be enhanced through additives or backbone modification, enabled by fiber morphology control.

[075] The process may proceed to step 190.

[076] As in step 190, the fiber may be manufactured into textile products via weaving, knitting, and/or other known processes. It is contemplated that the melt-spun polymer fiber may be utilized to manufacture textiles in substantially the same manner as a conventionally-used fiber thread (e.g., polyester, wool, silk, cashmere, cotton, etc.). Method 100 may be completed.

[077] **Polymer Fiber and Textile Characterization**

[078] While fiber aesthetics like “feel” and “drape” may be difficult to quantify via objective measurements, textile experts have developed a series of objective measures to describe fiber characteristics desirable in textile products. For example, with reference to FIG. 2, one fiber aesthetic property, Thermal Effusivity, is defined by ASTM test method 07984 and correlates with garment performance. Textiles may also be objectively characterized by measurements of the Kawabata Evaluation System. (See, e.g., <https://textiles.ncsu.edu/tpacc/comfort-performance/kawabata-evaluation-system/>) Such measures include compressional properties assessed by the KES-FB3 Compression Tester; bending properties assessed by the KES-FB2 Bending Tester; surface properties like co-efficient of friction and geometric roughness assessed by the KES-FB4 Surface Tester; and shearing and tensile properties assessed by the KES-FB1 Tensile-Shear Tester.

[079] “Scroop” is another aesthetic characteristic that describes a subtle, but undesirable sound typically generated by synthetic fiber fabrics when rubbed together between thumb and forefinger, but not by certain “noble” fiber fabrics, such as fine wool. Preferred embodiments of this disclosure

may result in protein-synthetic polymer fabrics that have no or negligible scroop—akin to natural, high-quality “noble” fabrics.

[080] Novel fibers disclosed herein may also be objectively characterized by filament size, cross-section measures, surface characteristics, fiber diameter, and/or the like. Additionally or alternatively, critical morphological parameters like crystallinity, molecular orientation, glass transition or melting temperature and dimensional stability may be used to characterize the novel nature of these fibers.

[081] Certain novel fibers disclosed herein may be characterized as having been melt processed to fibers of textile denier (1-30); containing up to 95% by weight of protein; containing at least 0.5%, 1%, or 2% by weight protein; and/or containing at least 0.5%, 1%, or 2% by weight keratin protein.

[082] **Melt Spin Fiber Generation Example #1: Filament Yarn**

[083] The following is an experimental example of generating a keratin containing filament yarn with superior aesthetics in accordance with method 100 (omitting steps 175, 185, and 190):

[084] Chicken feathers from Downlite were ground on a Restch centrifugal grinder, Model ZM200, with a .25mm screen at a rate of 5 lb/hr.

[085] The feathers were loosely packed in a pillowcase and dried in a column dryer with desiccated air of -40C dew point at 80C for 8 hrs. Polylacticacid polymer (Kinpoly HT101) was dried in the same column dryer.

[086] Polylacticacid was fed by precision feeder into a Leistritz 27mm twin screw extruder. The ground feathers were precision fed through a side feeder into the PLA melt at 10% by weight. The screw was configured for intense shear and mixing. The feather/PLA melt blend was extruded through a die into a water quench bath and pelletized. The pellets were dried in a column dryer with desiccated air at 65C and -40C dew point for 8 hrs.

[087] The pellets were fed from a hopper dryer into the hopper of a Hills melt spinning machine along with similarly dried PLA from the before mentioned source at a rate of 7.89% by weight.

[088] Yarn of 726.8/144 denier/filaments was wound up at 1060 m/min with a spinning temperature of 230C, a spinneret hole diameter of 0.6 mm and a maximum roll temperature of 85C.

[089] Approximately 0.25 lb was wound onto a bobbin. With reference to Fig. 4, an embodiment of melt-spun protein-synthetic filament wrapped on a bobbin is shown. It is believed that, unexpectedly, the melt-spinning process causes an increased proportion of the keratin

components of the composite to accumulate on the outside, exposed portions of the composite fibers than on the inside.

[090] The yarn from the bobbin was wound onto display cards approximately 4 in long by 2 in wide.

[091] Properties of the yarn were denier per filament of 5.04, tenacity of 1.24 g/denure, and elongation 21.3%. The fiber was a uniform light beige in color and had a translucent sheen judged more like a natural fiber such as silk than the characteristic shine of a synthetic fiber. The fiber was judged to have a more natural hand than that of synthetic fiber by fiber experts.

[092] **Melt Spin Fiber Generation Example #2: Filament Yarn with Controlled Crazing**

[093] The following is an experimental example of generating a keratin containing filament yarn with superior aesthetics in substantially accordance with melt spin fiber generation example 1, but with the addition of an embodiment of step 185. Specifically, in this example, a step of strain-induced crazing the surface of the filaments was added prior to yarn formation.

[094] The filaments of melt spin fiber generation example 1 were subjected to a high draw ratio to stretch break their surface—but not the entire fiber, referred to herein as controlled crazing. Although the controlled crazing technique may be known in the art for PLA fibers, the results of controlled crazing on the composite melt-spun protein-polymer fiber were unexpected. Specifically, after controlled crazing, the composite melt-spun polymer fiber/yarn of this example possessed aesthetic qualities nearly indistinguishable from silk.

[095] The resulting yarn was of very fine denier and could be characterized as a slip glide fiber. The inventors believe that controlled crazing of the composite changed the surface texture to expose more keratin elements of the composite and engender a softer feel. The yarn was woven into textile/fabric samples. Textile experts were largely unable to distinguish the fabric samples woven from composite melt-spun polymer fiber/yarn from similarly woven silk samples based on aesthetic appearance and feel.

[096] **Melt Spin Fiber Generation Example #3: Skin-Core Architecture Filament Yarn with Controlled Crazing**

[097] In another experimental example, keratin powder and PLA were compounded to obtain master batch pellets comprising approximately 40% keratin protein by weight.

[098] Skin-core architecture fibers were then melt spun using known techniques in the art. PLA without protein was extruded to form the core and the sheath was extruded from about 5-10%

masterbatch pellets and additional PLA pellets. The spun fibers were surface crazed then and twisted to form a filament yarn. The surface crazing was obtained via a solid state draw ratio of 4.1.

[0099] Each resulting fiber had a diameter of about 15 microns with expected tensile strength of at least 4 g/ denure and up to 5 g/ denure, based on the tensile strength measurements of example #4 .

[0100] The resulting yarn was of very fine denier and could be characterized as a slip glide fiber. The inventors believe that controlled crazing of the composite changed the surface texture to expose more keratin elements of the composite and engender a softer feel. The yarn was woven into textile/fabric samples. Textile experts were largely unable to distinguish the fabric samples woven from composite melt-spun polymer fiber/yarn from similarly woven silk samples based on aesthetic appearance and feel.

[0101] Although the skin-core architecture of fibers generated by this example #3 was not observable with conventional imaging, FIG. 7A reveals the skin-core architecture via Confocal Raman Microscopy. Protein particles on the outer surface of the fiber's sheath may also be observed in FIB. 7A.

[0102] FIGS. 6A, 6B, and 6C are SEM images of example #3 filament fibers at 200X, 500X, and 2500X magnification, respectively. With reference to FIG. 6A, it may be observed that the fibers are uniform and smooth, diameters consistent with measured denier. FIG. 6B depicts a filament fiber cross-section. With reference to FIG. 6C, surface crack morphology with approximately 1 micron spacing between the striations on the external surface of the sheath may be readily observed.

[0103] FIGS. 8A and 8D illustrate the EDX nitrogen and sulfur signatures, respectively, of fibers of this example #3. The stippled nature of the nitrogen and sulfur signatures indicates the presence of keratin on the outer surface as the PLA carrier lacks nitrogen in its composition. FIGS. 8C and 8F illustrate the EDX nitrogen and sulfur signatures of the keratin powder compounded with PLA to form the masterbatch (not shown) which was ultimately used to spin the sheath. The EDX data further confirmed that virtually all sulfur and nitrogen present in the powdered protein survived compounding into the master batch, and then survived fiber formation, treatment, and yarn formation, including extrusion above 200°C. This indicates that that the powdered protein in

the master batch survived the above described manufacturing processes without being gassed off and remained present and substantially intact in the protein-synthetic polymer yarn

[0104] FTIR – ATR results for this example #3 fiber appeared virtually indistinguishable with that of PLA, as shown in FIG. 9B. That is, FTIR-ATR analysis of example #3 did not evidence keratin presence, which was an unexpected result in view of keratin's signature (FIG. 9A) being reflected in compounded protein-synthetic polymer, as shown in FIG. 9C.

[0105] **Melt Spin Fiber Generation Example 4: Skin-Core Architecture Staple Yarn**

[0106] In this example, skin-core architecture fibers were spun in substantially the same manner as the filaments of example #3, but were subjected to a draw ratio of 3.2 in the solid state (about 25% less than that used in example #3), and accordingly did not possess surface crack morphology. The fibers were then crimped at approximately 12 crimps per inch, heat set at 130°C for approximately one minute, and then cut to form 45 mm fibers. These crimping parameters were selected to emulate wool.

[0107] Each resulting fiber had a diameter of about 15 microns; tensile strength of approximately 4 g/ denier, which approaches that of PLA; elongation of 32%; and Hot Air Shrinkage at 115 C of less than 5%. These properties are highly desirable for apparel application. The high strength along with the small fiber diameter permits small diameter yarns to have enough strength for knitting and weaving to fine fabrics. The tensile properties and shrinkage are superior to wool and are influenced by the carrier polymer and the process. The combination of superior tensile and shrinkage properties along with the soft, natural fiber feel is unique. Furthermore, fabric derived from this soft crimp, staple yarn had no substantially no discernable scroop (based on the ear of lay and expert observers), just like fine wool and unlike all prior art synthetic polymer fabrics known to the inventors.

[0108] Although the skin-core architecture of fibers generated by this example # 4 was not observable with conventional imaging, FIG. 7B reveals the skin-core architecture via Confocal Raman Microscopy.

[0109] FIGS. 5A, 5B, and 5C are SEM images of example #4 staple fibers at 250X, 500X, and 2500X magnification, respectively. As in FIG. 5A, it may be observed that the fibers are uniform and crimped, with diameters consistent with measured denier. FIG. 5B depicts a fiber cross section. And, in FIG. 5C, keratin protein particles of approximately 3 microns on the external surface of the sheath may be readily observed.

[0110] FIG. 8B and 8E illustrate the EDX nitrogen and sulfur signatures of fibers of this example #4. The stippled nature of the nitrogen signature indicates the presence of keratin on the outer surface as the PLA carrier lacks nitrogen in its composition. FIGS. 8C and 8F illustrate the EDX nitrogen and sulfur signatures of the keratin powder compounded with PLA to form the masterbatch (not shown) which was ultimately used to spin the sheath. The EDX data further confirmed that virtually all sulfur and nitrogen present in the powdered protein survived compounding into the master batch, and then survived fiber formation, treatment, and staple yarn formation, including extrusion above 200°C. This indicates that the powdered protein in the master batch survived the above described manufacturing processes without being gassed off, and remained present and substantially intact in the protein-synthetic polymer yarn

[0111] FTIR – ATR results for this example 4 fiber appeared virtually indistinguishable with that of PLA, as shown in FIG. 9B. That is, FTIR-ATR analysis did not evidence Keratin presence, which was an unexpected result in view of Keratin signature (FIG. 9A) being reflected in compounded protein-synthetic polymer, as shown in FIG. 9C.

[0112] **Additional and/or Alternative Embodiments and Enhancements**

[0113] It is contemplated that the above-disclosed protein-polymer mixtures may be used in a variety of other applications outside of the textile context. For example, in certain embodiments the extruded polymer may not be melt-spun into a 1D fiber (as in step 170). Instead, in certain alternative embodiments, the protein-synthetic polymer composition may be extruded into a 2D film for packaging or other applications via, for example, existing film extrusion technologies, such as high speed blown film machines. In other alternative embodiments, the protein-synthetic polymer composition may be formed into 3D products, such as bottles, toys, and other consumer goods via injection molding, stretch blow molding, 3D printing and/or other known methods of synthetic polymer molding. Such products would be expected to have unique surface properties.

[0114] Although the foregoing embodiments have been described in detail by way of illustration and example for purposes of clarity of understanding, it will be readily apparent to those of ordinary skill in the art in light of the description herein that certain changes and modifications may be made thereto without departing from the spirit or scope of the disclosure. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only,

and is not intended to be limiting, since the scope of the present invention will be limited only by its claims.

[0115] It is noted that, as used herein, the singular forms “a”, “an”, and “the” include plural referents unless the context clearly dictates otherwise. It is further noted that the claims may be drafted to exclude any optional element. As such, this statement is intended to serve as antecedent basis for use of such exclusive terminology as “solely,” “only,” and the like in connection with the recitation of claim elements, or use of a “negative” limitation. As will be apparent to those of ordinary skill in the art upon reading this disclosure, each of the individual aspects described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several aspects without departing from the scope or spirit of the disclosure. Any recited method can be carried out in the order of events recited or in any other order that is logically possible. Accordingly, the preceding merely provides illustrative examples. It will be appreciated that those of ordinary skill in the art will be able to devise various arrangements which, although not explicitly described or shown herein, embody the principles of the disclosure and are included within its spirit and scope.

[0116] Furthermore, all examples and conditional language recited herein are principally intended to aid the reader in understanding the principles of the invention and the concepts contributed by the inventors to furthering the art, and are to be construed without limitation to such specifically recited examples and conditions. Moreover, all statements herein reciting principles and aspects of the invention, as well as specific examples thereof, are intended to encompass both structural and functional equivalents thereof. Additionally, it is intended that such equivalents include both currently known equivalents and equivalents developed in the future, i.e., any elements developed that perform the same function, regardless of structure. The scope of the present invention, therefore, is not intended to be limited to the exemplary configurations shown and described herein.

[0117] In this specification, various preferred embodiments have been described with reference to the accompanying drawings. It will be apparent, however, that various other modifications and changes may be made thereto and additional embodiments may be implemented without departing from the broader scope of this disclosure. The specification and drawings are accordingly to be regarded in an illustrative rather than restrictive sense.

WE CLAIM:

1. A yarn, comprising:
 - a plurality of fibers, each fiber comprising protein and a synthetic polymer,
 - wherein:
 - each of the plurality of fibers comprises at least 0.5% protein by weight.
2. The yarn of claim 1, wherein:
 - each of the plurality of fibers is a melt-spun fiber.
3. The yarn of claim 2, wherein:
 - for each teach of the plurality of fibers, an outer portion has a higher density of protein particles than an inner portion.
4. The yarn of claim 2, wherein:
 - each of the plurality of fibers is a skin-core fiber comprising an inner core and an outer sheath.
5. The yarn of claim 4, wherein:
 - the outer sheath of each of the plurality of skin-core fibers comprises at least 1% protein by weight; and
 - the inner core of each of the plurality of skin-core fibers by weight comprises less than 1% protein by weight.
6. The yarn of claim 5, wherein:
 - each outer sheath comprises at least 35% of its respective skin-core fiber by weight.
7. The yarn of claim 6, wherein:
 - the inner core of each of the plurality of skin-core fiber by weight comprises less than 0.1% protein by weight.
8. The yarn of claim 2, wherein:

the protein is keratin or silk; and
the synthetic polymer has a melting point of less than 250°C.

9. The yarn of claim 4, wherein:

each of the plurality of fibers has a diameter of between 8 and 20 microns; and
an outer surface of each outer sheath includes a plurality of circumferential surface cracks.

10. The yarn of claim 9, wherein:

the plurality of circumferential surface cracks are spaced apart by between 0.5 and 2 microns.

11. The yarn of claim 5, wherein the yarn is a filament yarn.

12. The yarn of claim 1, wherein:

wherein the yarn is a staple yarn;
each of the plurality of fibers has a diameter of between 8 and 20 microns; and
each of the plurality of fibers has a length of between 20 and 128 mm.

13. The yarn of claim 4, wherein:

wherein the yarn is a staple yarn;
each of the plurality of fibers has a length of between 20 and 128 mm; and
an outer surface of each outer sheath includes a plurality of circumferential surface cracks.

14. The yarn of claim 13, wherein:

the plurality of circumferential surface cracks are spaced apart by between 0.5 and 2 microns.

15. The yarn of claim 12, wherein:

each of the plurality of fibers is crimped.

16. The yarn of claim 15, wherein:
each of the plurality fibers has between 5 and 20 crimps per inch.
17. The yarn of claim 15, wherein:
each of the plurality of fibers has between 9 and 15 crimps per inch.
18. The yarn of claim 15, wherein:
an outer surface of each outer sheath includes a plurality of circumferential surface cracks.
19. The yarn of claim 12, wherein:
the outer sheath of each of the plurality of skin-core fibers comprises at least 1% protein by weight; and
the inner core of each of the plurality of skin-core fiber by weight comprises less than 1% undenatured animal protein by weight.
20. A fabric comprising yarn, the yarn comprising:
a plurality of fibers, each fiber comprising protein and a synthetic polymer,
wherein:
each of the plurality of fibers comprises at least 0.5% protein by weight;
each of the plurality of fibers is a melt-spun fiber; and
the fabric has no or negligible discernable scroop to a human ear.