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Protein fibers: structural mechanics and future opportunities

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Abstract Part 1 of the paper reviews four categories of protein fibers. (1) Wool and other hairs, which have been used as textiles for thousands of years. (2) Regenerated protein fibers, which were manufactured in the 1950s but did not achieve continued commercial success, and, in the 1990s, fibers from artificially produced spider silk proteins. (3) Hagfish slime threads, as an example of other biological fibers. (4) Silks, from silkworms and spiders. In Part 2, stress–strain curves are compared and discussed in relation to what is known of the structure of the fibers and the mode of formation. Models of the structural mechanics are described. The possibilities for scientific and commercial advances in future are presented in Part 3.

Introduction

Proteins as textile fibers

In the middle of the 20th century, the dominant textile fibers were two cellulosics, namely cotton, which was the cheap general-purpose fiber, and linen, which had superior quality, and two protein fibers, namely wool, which was warmer and more durable, and silk, which was a luxury fiber but also the toughest available fiber, used, for example, in parachutes. The advances in chemistry near the end of the 19th century led to attempts to emulate silk and wool. The regenerated celluloses, rayon and acetate, were marketed as "artificial silk" and were followed, after the acceptance of the idea of macromolecules, by the synthetic fibers, acrylics, nylon, polyester and polypropylene. By 1975, polyester had become the dominant general-purpose fiber, and there was a new generation of high-performance fibers, which were recognized as emulating properties of another protein fiber, spider silk.

From 1935 onwards, the possibility of spinning artificial fibers from proteins was investigated. The thought was that these fibers would be more like wool than the regenerated celluloses. In the 1950s, *Lanital* from Snia and *Fibrolane* from Courtaulds were made of casein from milk; *Ardil* from ICI of ground nut protein; *Viacara* in USA of zein from corn. Soya bean protein was tried by Ford Motor company, and there were trials of many waste products, such as egg albumin, chicken feather protein, gelatin and silk waste. Today, if one puts *Lanital* into Google, one finds in a report on "Forgotten fibers" by Mary Brooks of the Winchester School of Art: *interest in these poorly performing* [regenerated protein] *fibers faded as they were overtaken by better quality synthetic fibers.* But hope is seen to spring eternal in another quote: *Today, research is motivated by both commercial and environmental concerns...the Chinese are hoping that soya bean protein fibers will reduce the number of cashmere goats, whose grazing accelerates desertification.* In the 1990's WRONZ (Wool Research Organisation of New Zealand) looked for a new use for coarse New Zealand wool, for which the market was declining. Fibers were dissolved and fractionated into the different proteins and other components. There was no commercial success in making fibers, but a market in cosmetic products was found for *Keratec* and there are expectations of medical uses. Xu et al. [1] have shown that

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better fiber properties can be achieved by spinning *Bombyz mori* silk from solutions in special organic solvents, such as *N*-methylenemorpholine-*N*-oxide (NMMO) and water. It is unlikely that these and other regenerated protein fibers will find a place in mainstream textiles, but there are opportunities in specialist areas, such as medical textiles with wound-healing or other desirable attributes.

From 1975 onwards, starting with the studies by R W Work at North Carolina State University, the outstanding properties of spider silk were recognised. In 2000, Termonia [2] wrote: *Spider dragline silk represents one of the strongest materials to date*...[and]...*is also characterised by a very high strain at break*. Unlike silkworms, spiders are not an easy source of harvestable fibers. However, advances in genetic engineering led to attempts to emulate spider silks. The first step, and this was thought to be the difficult step, was to produce spider silk proteins by genetic modification. DuPont were able to produce the proteins from a bacterial culture and Nexia from goat's milk. This led to early optimism on plans for super-strength fibers. DuPont had an advertisement in *Scientific American.* In 1999, there was a news quote from Nexia on *Bio-steel – the end product of a genetic marriage between spider and goat. Once Willow begins producing milk, Nexia will harvest it as the source of bio-steel...breaking strength of about 300,000 pounds per square inch* [2 GPa]. The reality was different. Three year's later, it was reported that Nexia and the US Army had spun the world's first man-made spider silk fibers, but they had low strength. In 2005, Nexia announced that they were moving away from traditional fibers to more specialised applications.

Experimental spider-silk fibers were no better than the regenerated protein fibers of the 1950's. The problem lay in the second step, making the fiber, which proved to be more difficult than making the proteins. As Vollrath [3] wrote presciently in 1999: *the next question...whether silk gene sequences have the high commercial value often claimed or whether more value should be attached to knowledge about the spider's production system. Personally I lean towards the latter.*

Biological fibers

Wool, hair and silks have a biological function. However, there are many other biological protein fibers, which are of interest in terms of their structural mechanics, though few have been investigated in detail. For example, equine hoof is a keratin fiber composite, collagen has connective roles, and mussel Bysuss threads of two types have a mechanical function.

Hagfish slime threads [3, 4], shown in Fig. 1, are dispersed from gland cells on the skin of this primitive fish and reinforce mucus to form a protective barrier when the fish is disturbed. They have unusual mechanical properties [5, 6], unusual amino-acid sequences in the intermediate filaments [7, 8] and an unusual mode of formation [3, 4]. More details will be given later in the paper.

Comparative mechanical properties

The range of mechanical properties of protein fibers is illustrated in Table 1. Wool is among the weaker textile fibers, but its strength is adequate for apparel and domestic textiles. Its high break extension, and hence fairly high energy to break, and good recovery properties lead to high durability. Particularly notable is its complete recovery, even from high strains, when wet or when wetted after dry extension. A regenerated protein fiber, such as *Fibrolane* from casein, is much weaker than wool, especially when wet, and has very poor recovery from dry extension. These are the reasons why the regenerated protein fibers lasted no more than a few years as commercial fibers. Silk is the toughest of the natural textile fibers as a result of its higher strength and fairly high break extension. It has good recovery properties. The newer fibers regenerated from silk in NMMO have reached strengths of 400 MPa, which is comparable to silk itself.

Spider silks have an enormous range of properties, depending on the particular function of the thread. The examples in Table 1 illustrate the very high strength of dry dragline silk, which has a low break extension and thus a very high stiffness, and, for wet capture thread, only slightly lower strength combined with extremely high break extension, giving a huge energy to break. Spider silk has good elastic recovery. Hagfish threads have high strength and high break extension, giving high energy to break. However, the extension is only elastic up to 30% extension and is then non-recoverable. Plastic deformation

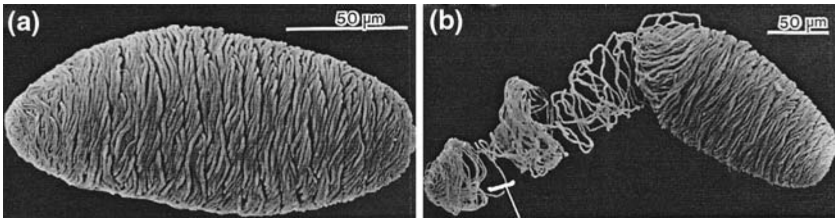

Fig. 1 Hagfish slim threads. From Koch et al [7]

Table 1 Typical values of mechanical properties

Fiber	Wet			Dry		
	Strength (MPa)	Break strain (%)	Elastic recovery	Strength (MPa)	Break strain (%)	Elastic recovery
Wool	130	60	100%[a]	180	40	50%[a]
Fibrolane	30	60	85%[a]	90	75	10%[a]
Silk *B. mori*	400	25	50%[a]	450	15	40[a]
Spider dragline				600	10	Good
Spider capture	550	500	Good			
Hagfish thread	200	250	Plastic above 30% extension	500	120	Poor

[a] From 10% extension

is unusual in natural protein fibers, but is no evolutionary disadvantage for hagfish. An intrusive attacker is more effectively caught up in plastic threads, which reinforce the mucus at a low concentration, than it would be by elastic threads.

Another feature of many natural protein fibers is supercontraction. Wool contracts by 7% in 7M lithium bromide solution and by 24% in a stronger solution. Gosline et al. [9] describe the 45% contraction of a spider silk when it is wetted. The causes of supercontraction are a randomising of crystalline structures and a breakage of hydrogen bonding or cystine cross-links. The resulting proteins are rubbery and are instructive in understanding the structural mechanics of the fibers.

Fiber formation and structural mechanics

General considerations

Protein molecules, which are a chain of amino-acid residues, –NH–CHR–CO–, achieve their diversity through the different sequences of 20 or more side-groups R of varying character. Hydrogen bonding occurs between –CO–NH– groups and there are other interactions, such as acid–base links, between side-groups. Two amino-acids are of special relevance. Proline, which forms a ring of $–CH_2–CH_2–CH_2–$ joining back and replacing –H in –NH–, distorts the shape of the chain. Cysteine $–CH_2–SH$ can change to cystine $–CH_2–S–S–CH_2–$, which forms cross-links within or between chains.

The molecules can take up two types of crystal lattice. These can be related to ideal forms that would be taken up by simple polypeptides with repetitions of a single simple side-group, such as –H or $–CH_3$. The amorphous globular forms are more diverse. The three basic forms, which are illustrated in Fig. 2, are:

- Coiled crystals, which approximate to Pauling's ideal α-helix, though there are both general deviations due to the size and activity of the side-groups and greater local disturbances due to particular side-groups. In intermediate filaments (IFs), such as the fibrils in wool, coiled coils form in multiple twisting of pairs from a dimer to the 32 molecules in the IF.
- Crystalline β-sheets, which may be partly distorted from the ideal form with fully extended molecules.
- A great many forms of globular molecules. In the simplest form, these would be random coils of flexible molecules, which act as typical rubbers. However, the interaction of particular amino-acid sequences can lead to specific forms, which are irregular but as deterministic as a crystal.

One of the miracles of nature is how genetics causes protein molecules to form in sequence and produce the complicated structures of which protein fibers are one example. We consider how the structure forms and determines mechanical properties in the examples: fibers

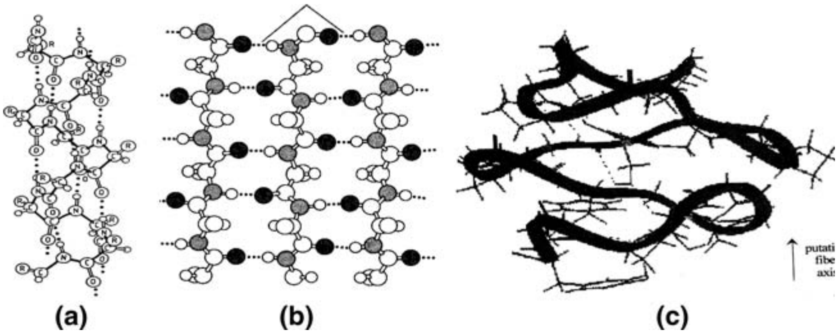

Fig. 2 Protein forms. (**a**) α-helix. (**b**) β-sheet. (**c**) An example of a globular form. Simulation of the GPGGSPGGY peptide unit in spider silk [10]. The amino-acids and side-groups R are: G = glycine, –H; P = proline, $–CH_2–CH_2–CH_2–$; S = serine, $–CH_2OH$; Y = tyrosine, $–CH_2C_6H_60H$

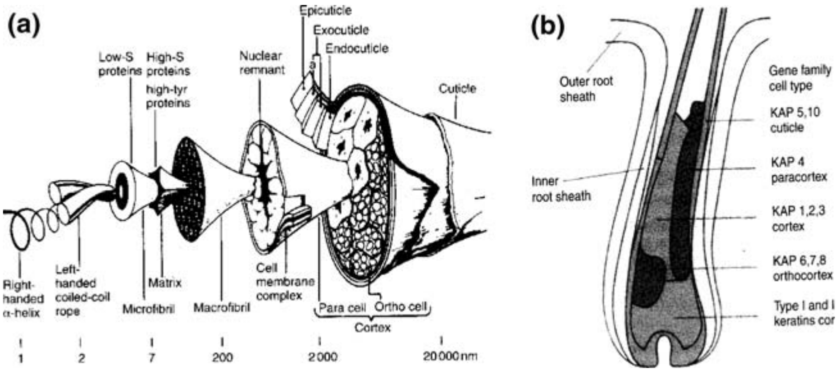

Fig. 3 (**a**) Wool fiber as drawn by Robert C Marshall, CSIRO. (**b**) Expression of proteins along the hair follicle [11]

regenerated from solution; wool and hair; hagfish slime thread; spider silk.

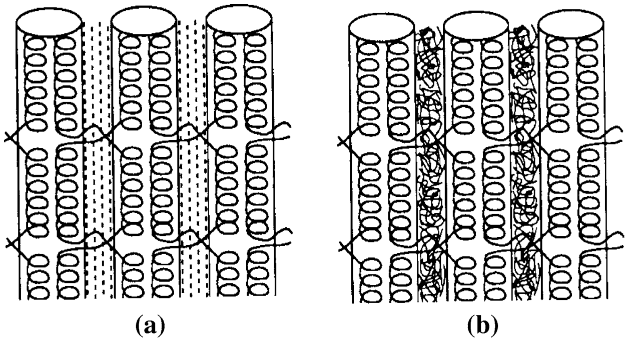

Fig. 4 Possible mode of formation of fine structure of hair. (**a**) Keratins form helical IFs separated by the head and tail domains. (**b**) The KAPs fill in the matrix, which is later keratinised as cysteine converts to cystine

Manufactured fibers

In the wet state, regenerated fibers, whether of the proteins used in the 1950's fibers or genetically engineered spider silk protein, have a weak rubbery network with low break stress, high extension and good recovery. In the dry state, a hydrogen bonded network gives initial stiffness followed by yield and poor recovery. This behavior is not surprising if the source was a globular protein, which is coagulated in spinning, partly oriented by stretching and stabilised by formaldehyde cross-links. If the source was a strong natural fiber, the biological structure is lost and cannot be usefully re-formed.

Wool and hair

Wool and hair have structure at many levels, as illustrated in Fig. 3a, which are formed in sequence as the hair grows out of the follicle, Fig. 3b. The type I and II keratins in the intermediate filaments (IFs)[1] are produced first, followed by the keratin-associated proteins (KAPs) of the matrix, and then the KAP of the cuticle. The keratins in the IFs, which give the α-helical rods, also have head and tail domains, which extend into the matrix. A possible mode of formation is shown in Fig. 4. A parallel assembly of fibrils is later filled in by a matrix.

There are complexities of chemical and physical structure [11] that are too extensive to repeat here, but certain features are specially significant for mechanical behavior; others require more study. Both the KAPs and the keratin head and tail domains contain considerable cystine, which gives the matrix the character of a cross-linked rubber. At a larger scale, wool and hair are bicomponent structures with ortho- and para-cortex cells. In the para-cortex, the fibril–matrix composite is oriented parallel to the fiber axis. In the ortho-cortex, the fibril–matrix composite forms a helical array in macrofibrils. The reasons for the difference are not known. It may be relevant that the ortho-cortex matrix contains more KAPs rich in glycine–tyrosine. A developing theory suggests that the occurrence or absence of twist in the macrofibrils may result from differences in chirality (A. J. McKinnon, private communication).

A full model of the mechanical properties of wool and hair involves all the levels shown in Fig. 5, but only two aspects will be mentioned here.

The crimp of wool, which gives it bulk, results from the bicomponent structure. When the fiber dries, the matrix shrinks. In the ortho-cortex, this reduces the helix angle so that the macrofibrils want to increase in length, whereas in the para-cortex the length is unchanged. In the simplest case of a side-by-side bicomponent fiber, the balance between the two effects causes the fiber to bend and results in a helical crimp. Other distributions of ortho- and para-cortex behave differently, which is why some hair is straight and some is curly.

The stress–strain behavior of wet wool, shown in Fig. 6, is remarkable for the complete recovery from large strains,

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[1] There is dual terminology depending on whether the emphasis is on the biological structure or the mechanical model. Intermediate filaments (IFs) are also called rods, fibrils or microfibrils. Keratin-assocaited proteins (KAPs) make up the matrix.

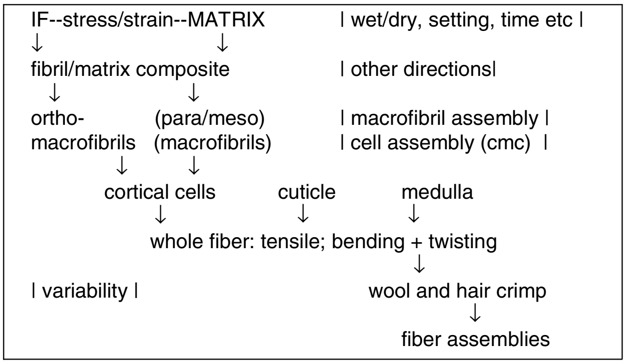

Fig. 5 Levels of structure for mechanical modeling of wool and hair

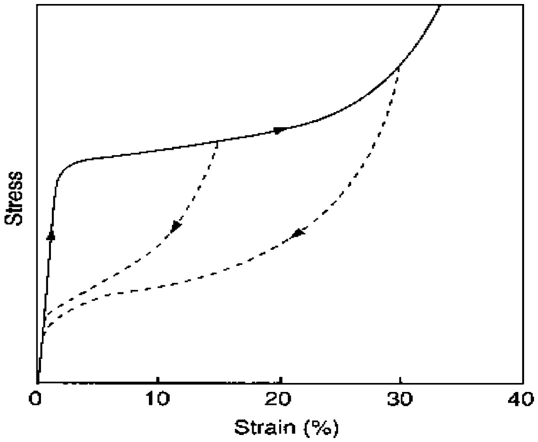

Fig. 6 Stress–strain curve of wet wool in extension and recovery

but on a different line to the extension. There are currently two models in contention, with a third unlikely possibility [12]. All the models agree that, although there will be influences from higher levels, the stress–strain curve depends primarily on the response of the fibril–matrix assembly. The disagreement is on the properties and hence also on the composite mechanics. The Chapman/Hearle [13] model assumes that the $\alpha \leftrightarrow \beta$ transition is controlled by a critical and an equilibrium stress, that the matrix follows a rubber-elasticity curve, and that there is stress transfer from fibril to matrix as zones (cf Fig. 4) open to 30% extension in the yield region. The Wortmann/Zahn [14] model assumes only an equilibrium stress for the $\alpha \leftrightarrow \beta$ transition, that the matrix is a thixotropic gel, and that the stress–strain curve depends on sequential opening of the IF segments. There are supporting arguments and problems for both models.

Hagfish slime threads

Hagfish slime threads, which are illustrated in Fig. 1, are formed within epithelial cells on the skin of the hagfish. When a hagfish is disturbed, the cell membrane breaks open, thread is ejected together with mucus and forms a slime in a large protective volume round the hagfish. Except that the L12 segment is slightly longer, the central rods of the hagfish protein have the same numerical sequence of amino-acid residues as other intermediate filament proteins, notably keratin in wool, but the actual amino-acid content is almost completely different [7, 8, 11]. The head and tail terminal domains are also different in composition and notably contain no cysteine to form cystine crosslinks. There are no keratin-associated proteins to form a matrix.

The threads, which are about 1.5 μm in diameter, varying somewhat along the length, are produced within the cells and wound up as ellipsoidal balls, which fill the cells. The "package production" is analogous to the way in which rayon was produced until around 1950 by winding up on the inside of a drum to form a "cake". The synthesis is probably virgin polymerisation, in which amino-acid residues add on to the molecules that form the dimers, which assemble into complete intermediate filaments and then into the whole thread. This mode of formation is completely different to the multicellular formation of wool or the extrusion of silks.

Fudge and Gosline [5] postulate a structure of an α-helical central rod in series with the terminal domains, as illustrated in Fig. 7a. Neighbouring dimers overlap as in Fig. 7b. The interaction between successive molecules will be weak, but it is likely that the multiple twisting in the layers of the intermediate filament will provide cohesion, much as in a textile yarn [15]. The stress–strain curve of the thread is shown in Fig. 8a with the zones identified by Fudge et al. [6]. In contrast to other natural threads, the deformation is plastic except for the small region of initial elastic deformation. As mentioned above, this is an

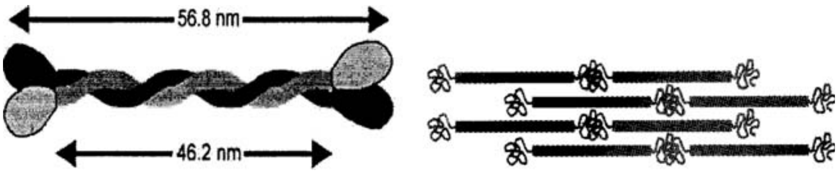

Fig. 7 Molecular model hagfish slime thread protein with central rod and terminal domains in series, from Fudge and Gosline [5]. (**a**) Dimer. (**b**) Overlap as dimers build up to 32 molecules in the intermediate filament

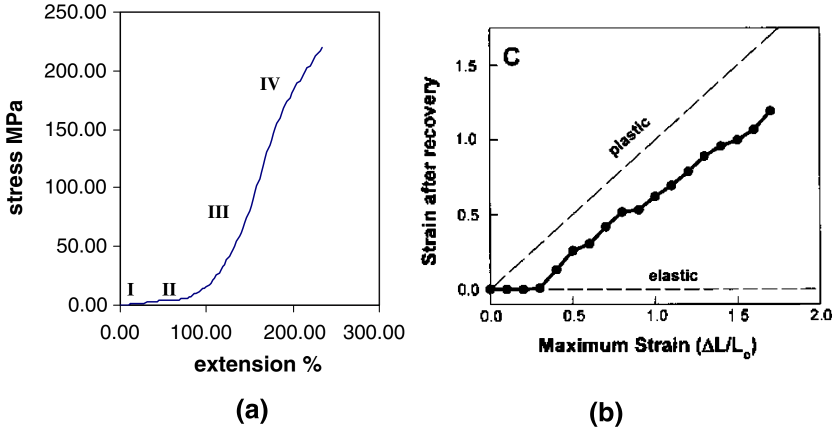

Fig. 8 (**a**) Stress–strain curve of wet hagfish slime thread. (**b**) Division into elastic and plastic deformation. From Fudge et al. [6] and Fudge and Gosline [5]

evolutionary asset. The dry stress–strain curve [5] shows an initial high modulus leading to yield at 130 MPa and 2.5% extension. The curve then rises roughly parallel to zones II, III and IV of the wet stress–strain curve to break at 450 MPa and 120% extension. This response is typical of hydrogen-bonded systems.

A series mechanical model contrasts with the parallel models of wool, which are discussed above. Interpretation of the molecular and structural basis of the stress–strain curve is still speculative [15]. The shape of zones III and IV is similar to the response of a rubber and is plausibly attributed to the terminal domains, which are assumed to have an irregularly coiled configuration. However, in the absence of cross-links, the extension is effectively the uncoiling of single molecules, albeit as head and tail domains attached to central rods. If this is modeled as a chain of flexible links using the inverse Langevin function form for rubber elasticity, the shape is right but the predicted stresses are orders of magnitude below the measured values. An alternative explanation is that the uncoiling is dependent on free energy as the minimum energy coil is pulled into less favorable conformations. Because both models depend on changing angles along the chain, the shape of the curve should be similar. This mode of deformation would be plastic as found experimentally. The reduction of slope in zone IV is typical of the breakdown of elements of the structure of polymer materials.

Other biological fibers

The mechanical properties of a number of other natural fibers have been studied and two examples can be mentioned. Mussel attachment threads have a distal region with a stress–strain curve similar to wool and a proximal region of lower stress and higher extension [16]. Equine hoof is a composite structure with stress–strain curves similar to wool [17]. Modeling the structural mechanics of these and other biological fibers would add to understanding of natural connective tissues.

Spider silks

In addition to the differences from other silks, such as textile silk from a silkworm, spider silks exist in a great variety of types with a wide range and variability of mechanical properties as illustrated in Fig. 9. The notable features are the strength, which can be comparable to aramid fibers, and high or extremely high extensions. There is an extensive literature on the subject and only brief, speculative comments can be made here.

The amino-acid composition is relatively simple with large amounts of glycine (–H) and alanine (–CH_3). A moderate amount of proline with its ring structure linking adjacent main-chain atoms will influence the form of coiling (see Fig. 1c). The degree of crystallinity is of the

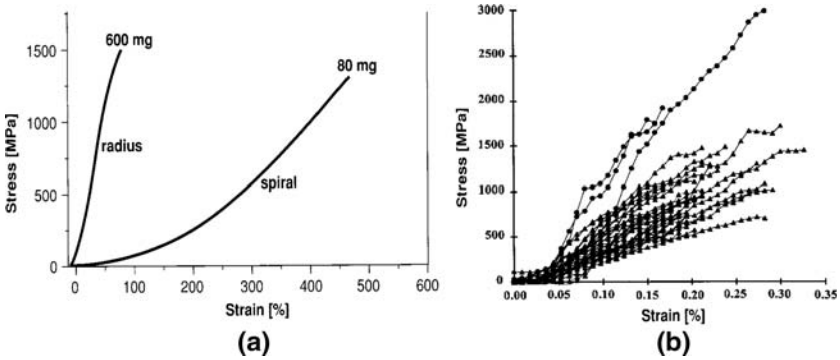

Fig. 9 of spider silk properties. (**a**) *A. diademus*. "Radius" is dry dragline; "spiral" is wet capture thread [18]. (**b**) *L. Hesperus* scaffolding silk [19]

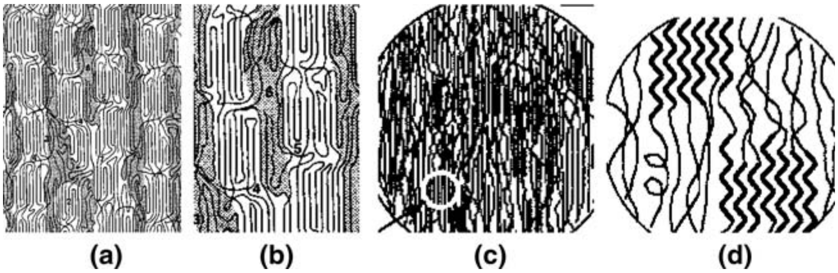

Fig. 10 (**a**, **b**) A suggested structure for nylon [20]. (**c**, **d**) A suggested structure for spider silk [21]

order of 50% and specifying models of structure has the typical difficulty of describing partly ordered systems. As illustrated in Fig. 10 speculative models of spider silk [21] are somewhat similar to those for nylon [20]. There is molecular continuity between crystalline regions, β-sheets for spider silk, and less ordered regions. However, there are important differences. Firstly, in spider silk, there is no folding back of the chains, except in small localized ways, whereas, in nylon, there is major reversal of direction in folds at the edge of crystals or in amorphous regions. Secondly, in spider silk the molecules are assembled in matched lengths, so that they are all close to the fully extended state when failure occurs. As with nylon, the extensibility comes primarily from stretching of molecular segments in amorphous regions, but due to good load sharing premature rupture of tie molecules is avoided. In supercontraction [9], there is a re-arrangement, which leads to rubber-like behavior.

How do spiders achieve such remarkable structure and properties? The proteins are synthesised in gland cells and copolymerisation determines the silk type. In order to form the structural features described above, the chains must grow by virgin polymerisation and assemble in parallel with no major disarrangement being allowed at any stage of thread formation. The filaments are drawn through the cell walls, which may act as "nano-spinnerets" by an "engineering drive" into where, according to Vollrath [22]: *This silk precursor then moves through a production line where it assembles or is assembled. Somewhere along this line is a valve or clamp to squeeze the silk, to hold it in place, or to forward it to the spigot and, in the case of some silks, to grip in order to allow the spider to dangle from it during abseiling and moulting.*

Ways forward?

Scientific advance

As Vincent [23] said in 2003: *Most protein fibers are still inscrutable mechanically. We do not know enough to be able to derive useful materials using the information available about amino-acid sequences or the implications of that sequence for the generation of all but the simplest secondary and tertiary structures.* This may be a little too pessimistic. As partly described in this paper, there are ways of developing reasonably robust models on the basis of present knowledge. However, this is only a first step. Fundamental advances are also needed. The need is to bring the amount and quality of mechanical modeling to the level achieved over the last 50 years in genetic science and engineering, proteomics and techniques for studying structure. Although the structure of both the helical portions of intermediate filaments and the crystalline regions in silk have been extensively studied, so that they are now well known, we lack information on the structure of the less ordered regions, namely the matrix of wool, the terminal domains of hagfish slime threads, and the amorphous part of silks. This is unfortunate because, although the ordered regions provide stability to the fibers and the special feature of the elongation in the $\alpha \leftrightarrow \beta$ transition, the nature of the deformation and the stresses developed are highly dependent on the less ordered regions.

Advances are needed both experimentally and theoretically. Special analytical techniques may help to demonstrate the nature of the structural changes in deformation, which provide guidance to modeling. X-ray diffraction will be helped by the new, more powerful, synchrotron sources being built. Raman and infra-red spectroscopy and the advances in electron and atomic force microscopy provide other tools. The greatest opportunity would come from the application of dynamic molecular modeling. This has been used for structural studies [24, 25] and thermal transitions [26]. Although the commercial computing packages contain deformation facilities, these do not appear to have been used to study proteins. The problem with this form of computational modeling is that the size of system that can be modeled is limited by the time needed to equilibrate, time available to run the model and computer power. Ideally one would like to model a whole intermediate filament interacting with terminal domains and matrix or a volume of silk containing a number of crystalline regions. This is clearly impossible at present. Even a dimer is too big. However, it should be possible to model short segments of an IF protein or limited repeats of globular proteins. These could then be linked together by simple mechanical models and lead on to total models, such as the sequence shown in Fig. 5, where the mechanics at higher levels is understood.

Practical opportunities

What are the ways forward for protein fibers in technological advances with commercial potential? Table 2 summarises the past and present situation for the four types of protein fiber, with which this paper has been concerned.

Wool, which has been used for thousands of years, changed in the last 50 years from a commodity fiber to a more specialist fiber aiming at a more expensive market than the commodity synthetic fiber, polyester. Its slow production is suited to agriculture and the complexity of the fiber means that a biomimetic alternative is impractical. There are possibilities of incremental advances in quality, particularly if a research programe of genetic engineering was carried out. However, the most important way forward for wool is to improve the links between the wool grower, the textile manufacturer and the market. The traditional route for wool into salerooms would be better replaced by wool of the required character being produced to meet specific market opportunities. The search for new uses of wool, particularly the coarser wools that are a by-product of meat production, will continue.

Unless there is some unexpected invention, the regenerated protein fibers, which can be produced at an economic rate, cannot achieve the performance needed for mainstream textile use. It may be that they will find applications in some specialist areas, such as medical textiles, where their natural origin may be beneficial.

Neither hagfish nor spiders are likely candidates for farming, although attempts are being made to milk spiders to produce thread for special purposes. The biomimetic possibilities will be covered in the next two sections.

Hagfish thread biomimetics

Hagfish slime thread has properties suited to the use for which it has evolved, but its properties are poor for commercial use. Plastic deformation is not attractive for most applications. This is not an insuperable problem, because genetic engineering could combine the genes responsible for the mode of formation in coils inside a cell with expression of proteins with the amino-acid sequences that would give a range of fibers with properties needed for particular applications. The question is how could this be exploited in large-scale production.

Blue-sky thinking suggests that this might be achieved by artificial cell cultures. If the gland cells can be cultured, they would reproduce and form the internal coils of thread. Mature cells would move to the next production stage and be triggered to burst and release the thread. There would then be a need for a textile operation to collect the threads and assemble them into yarns, which could be wound up at a reasonable rate.

Spider silk biomimetics

It has been demonstrated that genetic engineering can reproduce spider silk proteins with the bacterial route pioneered by DuPont probably commercially superior to the use of goats by Nexia. However, simple solution and spinning of these proteins failed to produce useful fibers for reasons discussed above. The assembly of the protein chain molecules is critical. The composition of the proteins is less important and it may be that simpler analogues of the spider silk proteins could be used. Design of the proteins could be adapted to the needs of particular applications. The problem is to find a way of spinning useful fibers. A possible biomimetic route is probably less directly biological than the cell culture suggested for hagfish slime thread. The critical need is for virgin polymerization followed by assembly of the molecules in matched lengths.

Virgin polymerization, which is the continuous addition of polymers to growing chains in an organised way, occurs naturally in living systems. For example, cellulose molecules grow on enzyme complexes in cotton and other plant fibers and are laid down in helical arrays on the cell walls. Smith et al. [27, 28] developed the virgin polymerization of polyethylene as a way of making high strength, high

Table 2 Current summary and ways forward, with ratings on a scale of 10

	Wool	Regenerated protein fibers	Hagfish slime thread	Spider silk
History	10,000 yrs (use)	70 years (production)	10 years (study)	30 years (study)
Production rate	meter/year	meter/second	meter/day	meter/min
Direct exploitation	10/10	10/10	0/10	1/10
Performance	8/10	1/10	1/10 → 10/10 ?	10/10
Incremental advance	5/10	2/10	0/10	0/10
Other uses as made	2/10	5/10	1/10	2/10
Biomimetic	0/10	N/A	5/10 ?	5/10 ?

modulus fibers, but this was not justified for commercial use in competition with gel-spinning. Although only suited to laboratory production of small amounts, the techniques used for collecting and drawing the material may be a guide to larger-scale methods. Films of the virgin polymer were collected on glass slides and then drawn on an Instron tester. Strengths of more than 3 GPa were achieved at a lower modulus than gel-spun fiber.

Blue-sky thinking envisages virgin polymerization of appropriate amino-acids on enzyme complexes or catalysts, which must then be assembled in bundles (nano-filaments) in matched lengths. The bundles might be drawn through nano-spinnerets, after an operation analogous at a much smaller scale to the threading of yarn on a texturing machine. They would then be assembled in larger bundles (yarns) and wound up at a commercial speed. The critical requirement, after polymerization would be to avoid significant disarrangement of the molecular bundles.

Conclusions

The following conclusions can be drawn from the review of protein fibers in this paper.

- In nature, there exists an incredible variety of protein fibers tailored—and tailorable—to purpose. Three examples, plus artificially manufactured fibers, illustrate the diversity.
- Wool, other animal hairs and silk have a future as quality fibers matched to commercial needs. This has implications for the industry in terms of linking growers to markets so as to produce fibers with the qualities needed for particular applications.
- Solution spinning of proteins may meet some special uses, e.g. medical applications, but is not a viable route for the production of fibers with good mechanical properties.
- Genetic engineering opens up new possibilities.
- Protein chemistry, the production of the proteins found in nature, is not in itself enough to mimic spider silk and other natural fibers.
- Fundamental understanding and imaginative invention might lead to biomimetics of hagfish threads and spider silk.
- Mechanics has lagged behind genetics, proteomics and structural analysis in scientific advances of biological materials in the last 50 years.
- There is a need to understand structural mechanics, in order to provide the link from formation to performance. This is of much wider biological and medical significance than just the study of fibers.
- The fibers described provide valuable model systems, because it is easy to measure their properties in a variety of states.
- Clever experiments should be carried out to determine the changes in structure during deformation.
- Dynamic molecular modeling, based on atomic interactions, should be applied to increase understanding of the mechanical behavior of protein systems. Clever ways need to be used to overcome the limits of computing power.
- Inputs from molecular modeling will feed into total mechanical models of fibers at what are often many structural levels between atoms and whole fibers.

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