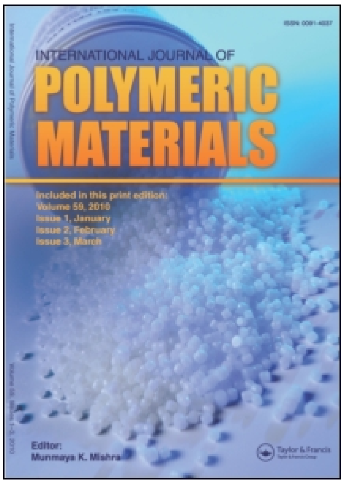

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Technology of Strong Fibers: Where are We and Where Should We Direct Our Investigations?

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The predictions of future successful technological developments are an important task of research organizations. The extremely poor reliability of these predictions has eroded trust in the efficiency of research laboratories which, in turn, resulted in substantial decreases in and availability of research funding. The causes of poor prediction relability are discussed and ideas are presented on how to minimize this problem. By applying the presented methodology, it is shown that, in the case of strong industrial fibers, we can learn a great deal from evolutionary processes of silk fiber formation and utilize this knowledge to solve some critical environmental problems of current man-made fiber production.

INTRODUCTION

The prediction of future technological developments is one of the most relevant and, at the same time, the most risky task of research organizations. Accurate predictions can bring research teams enormous financial rewards, while the wrong ones frequently lead to the dismantling of very competent and dedicated teams.

Since inaccurate predictions greatly outnumber accurate ones, it is desirable to discuss which outcomes are predictable and which are not. From this point we can identify three different areas of technological research.

(1) Research based on unexpected discoveries which represent a major technological breakthrough that could not be predicted by existing theories.

(2) Research directed at solving some key problems of current products (User-driven research).
(3) Research based on recent technologically not yet exploited scientific discoveries. (Science-driven research).

Since the major issue in this case is the neglect of or disrespect for quantitative assessment of technological probability of success [TPS], it is desirable to review TPS data compiled during last 35 years of industrial research.

(1) Real technological breakthrough: TPS = 0
(2) Market driven research:
    (a) New products: TPS = 0.05 − 0.01[1]
    (b) Product improvements: TPS = 0.30
(3) Science-driven research TPS = 0.005[1]

Examples of false analogies that led to large futile research efforts are listed below:

Cross-linking of cotton	Cross-linking of man-made fibers
Blending of plastics	Blended fibers and films
LC plastics and fibers	LC films
Adhesion of tire cords	Adhesion of fibers
Surface mod. of textile fibers	Adhesion of ultra-strong PE
strength Compressive strength of fibers	Transverse properties
Molecular reinforcement with LC polymers	Role of annealing

SCIENCE-DRIVEN RESEARCH

Based on this background we will focus our forecasts on research prompted by scientific discoveries and seek areas of overlap with user-driven research.

[1]The main reason for disappointingly low TPS of forecasts in these areas lies in the false analogies, because the successes in one case are unjustifyingly generalized and applied to other cases.

The advantages and disadvantages of natural fibers over man-made fibers are well known to those skilled in the art. The attempts to borrow from nature to upgrade our wiry man-made fibers have frequently led to tangible textile product improvements, especially in areas such as comfort, hand, crimping and aesthetics. In the area of strong industrial fiber technology, borrowing from the vast field of natural fiber science has so far failed to make a tangible contribution. One of the scopes of this article is to show that an overview of intriguing silk fiber manufacturing by spiders indicates several heretofore unexplored or unexploited opportunities for advancing strong fiber technologies.

To assess the state of the art of strong man-made fibers it is important to compare the steps and problems in the preparation and use of polyethylene fishing nets with the preparation of spider webs.

Steps and problems of manufacturing and use of ultrastrong PE fishing nets:

(1) Preparation of polymers (ecological problems)
(2) Manufacturing of basic fiber (ecological problems)
(3) Modifications of basis fibers to achieve desirable properties of yarns
(4) Design of fishing net system
(5) Fabrication of fishing nets
(6) Fishing (ecological problems)
(7) Transport, marketing and selling of catch
(8) Regeneration of raw materials for polymer synthesis.

It is important to note that the various phases of fish net manufacturing and use require not only specific knowledge of various technical disciplines such as: polymer chemistry, chemical engineering, mechanical engineering, polymer physics and polymer processing, but also the participation of several groups of specialists as well as transport of intermediate products to locations where the subsequent phases of the process are carried out.

It is, therefore, most surprising that the spider is capable of carrying all these processes by himself at technological levels that surpass by a wide margin the levels of our cutting edge technologies. It will be shown that, in the technology of hunting nets, the skills of a single primitive creature outperform the accomplishments of the numerous scientists and engineers who brought the technology of polyethylene nets to the present levels.

ARCHITECTURE OF SPIDER NETS

Spider webs are used in a broad range of applications from reinforcement of terrestrial burrows to aerial orb webs for catching insects. These hunting nets are two or three dimensional and are constructed with fibers having very different mechanical properties. The manufacturing of these architecturally complex and, from a mechanical engineering point, most advanced net systems is possible because of the ability of spiders to prepare fibers and yarns having a wide range of properties. The common garden spider is able to produce 7 different silks that include: (1) drag line, (2) structural thread, (3) capture spiral fibers and (4) aqueous and glycoprotein glue for capture spiral [1].

Spider webs have an outstanding capability to absorb out of plane impact and aerodynamic energies. This energy-absorbing capability does not depend only on the material properties of web components but also on the construction of the web. Mechanistic studies of web design have shown that, from the point of engineering mechanics, these designs are optimized to levels that cannot be surpassed by present design tools and methods.

Although the orb webs of spiders contain several components, we shall limit our discussion to two: the radial supporting yarns and the interradial capture threads. The respective mechanical properties of these two components are presented in Figure 1 [1]. The firm radial components which transmit vibrations indicating the presence of an insect, contribute to the structural integrity of the system and also represent the path on which the spider moves around the net. The capture spiral thread, however, is viscous, sticky and extraordinarily elastic. Some spiders have also the capability to produce crimped thread that acts as a spring. The process the spider uses to impart the crimp to the straight filament is an analogue of knife-edge crimping, a process that has been used for the preparation of elastic hosiery yarns. It is interesting that this process is very time consuming when carried out by fibers and man. A much more elegant system involves a windless system which takes advantage of simple physical forces that exist in droplets of viscous glycoprotein containing ball shaped packets of bunched fibers [1].

In regard to architecture and design of spider nets and the preparation of cord systems with a broad range of technology, the

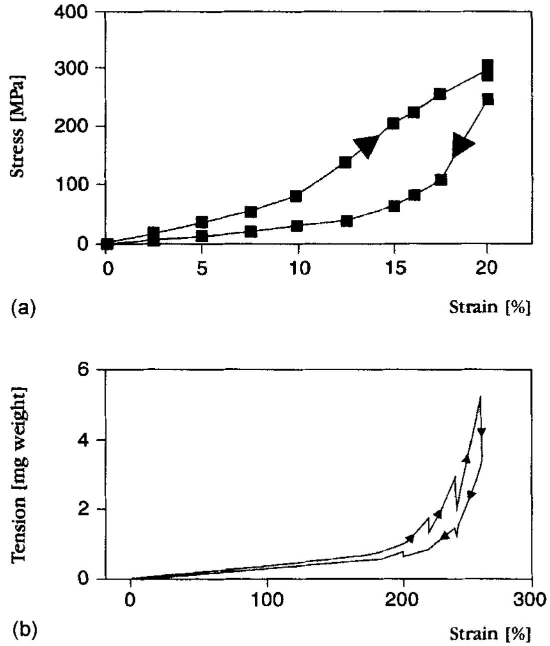

FIGURE 1 Tensile properties of drag and capture fibres [1].

optimization through evolution brought the spider capabilities relative to the properties achieved at the cutting edge or even beyond levels of present man-made fiber technology. The important advantages of silk fiber manufacturing lie, however, in the pollution free silk preparation processes, energetics of the process, and the ability to digest the silk for respinning and food.

CHEMICAL COMPOSITION AND MANUFACTURE OF SILK FILAMENTS

Based on the sequence analysis of nucleic acids it was concluded that spider silk contains more than one protein. In specific cases this number is limited to two. The analysis of the materials in the gland ampules and in the silk shows that the chemical composition of these two materials is identical. The analysis also shows that the silk proteins consists of amino acid sequences that can occur with 80–100% homology from about ten times to more than fifty times.

The most important amino acids in these repeated sequences are:

Glutamic acid	GLA
Glycin	GLY
Serin	SER
Arginine	ARG
Alanine	ALA
Proline	PRO
Tyrosine	TYR
Leucine	LEU
Glutamine	GLN
Cystein[2]	CySH

For example, a type of drag line contains a protein consisting of 53 or 34 repeating sequences of the following structure [2]

-TYR-GLY-LEU-GLY-SER-GLN-ALA
-GLY-ARG-ARG-GLY-GLY-

These repeating sequences enable the unordered silk proteins to spontaneously form ordered domains, domains that stabilized with disulfide (cystein) bonds are capable of spontaneously assuming supermolecular structures responsible for the nematic character of aqueous solution from which the silk is spun.

TABLE I Typical strong fiber properties [4]

Fibre	*Modulus (Gpa/gpd)*	*Strength (Gpa/gpd)*	*Elongation at break* (%)
Major ampulate gland *N. clavipes*			
Spider silk	22/190	1,1/10	9
High tenacity nylon	5/50	0,9/8,7	18
Industrial polyester	15/125	0,9/7,5	13
Kevlar 29	62/520	2,8/22	3,5
Kevlar 49	124/1040	2,8/22	2,5
Spectra 1000	171/2000	3,0/35	2,7
High Modulus Graphite	393/2394	2,6/15,8	0,6

[2]Important for disulfide bond which prevents premature precipitation.

Properties of Spider silk and various man-made fibers are presented in Table I [4]. Considering that the outstanding properties silk fibers are achieved without a postextrusion treatment, at ambient temperatures and using water as solvent we must conclude that in regard to polymer synthesis and fiber fabrication the spiders are way ahead of the state of the art man-made fiber manufacturing.

CHARACTERISTICS OF CRYSTALLINE PHASE OF SILK

Based on present knowledge of oriented polymer preparations, it can be inferred that the silk fiber mechanical properties presented in Table I are, without post extrusion stretching, achievable only with nematic solutions. Note also that the properties reported by Zemlin [5], (30 Gpa modulus and 1.9 Gpa strength are 50% higher than those reported by Cunniff *et al.* [4]. Viney *et al.* [3] systematically investigated the properties of the liquid crystalline phase by means of transmitted polarized light microscopy in various silk of many spiders as well in reconstituted silk solutions. In principle, light microscopy along cannot provide insight into the characteristics of domains responsible for the nematic behavior. With the use of Flory's phase diagrams, however, these authors succeeded in determining the basic characteristics of globular peptides and their rod-like aggregates responsible for the critical performance in the key phases of silk fiber formation which include: (1) solubility of fibroin in water, (2) easy transport of solution though ducts and orifices and (3) shear induced orientation of rod-like aggregates in the last phase of the process which results in the high modulus and strength of silk fibers.

The structure of three phases of silk formation proposed by Viney *et al.* are schematically presented in Figure 2a, b and c. It is important to note that globular molecules of fibroin in the glands can, without conformational changes, form rod-like units. The essential characteristics of the liquid crystalline state of aggregation is that:

(i) the polymer retains its solubility because the solvent (*i.e.*, water) sees the same groups on the surface of the agglomerate as on the globules,

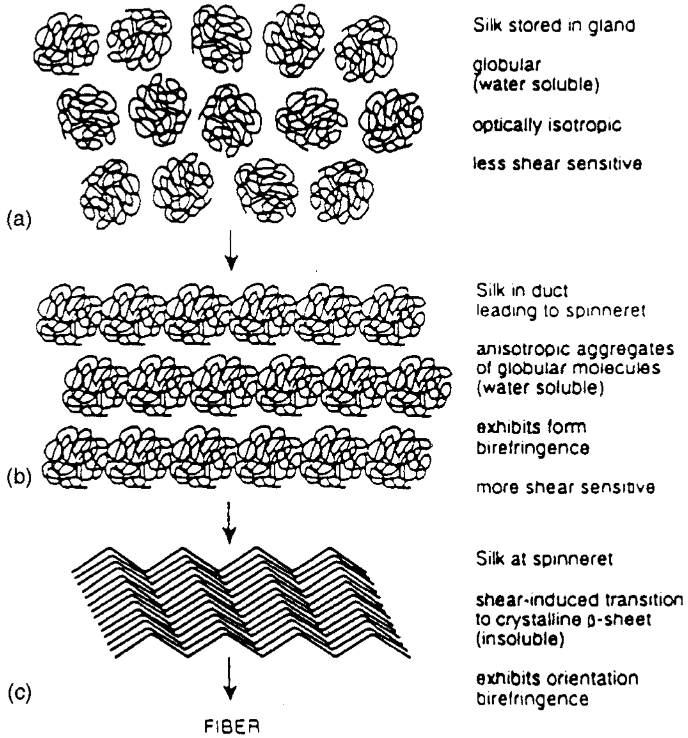

FIGURE 2 Molecular order of silk secretion in various stages of fibre spinning [3].

(ii) parallel to this effect, the nematic structure of the solution leads to a reduction in viscosity, allowing easy transport through the ducts and orifices, and

(iii) spinning at above critical speeds causes the aggregates to be stretched and crystallized into insoluble beta-foils.

CONCLUSIONS

(1) It has been shown that predictions of meaningful technological developments are very uncertain and that we have at present no ideas or hopes that this situation can be improved.

(2) Despite the principle obstacles to preparing reliable forecasts, research laboratories must develop forecasts to engage scientists in the fields of interest.

(3) Contrary to the beliefs that strong man-made fibers represent a mature technology, major advances can and will be made by borrowing from natural fibers.
(4) The presented review of silk fiber formation shows several areas where significant advances in man-made fiber technology can be made by utilizing sophisticated structures of evolutionary biopolymers and biopolymeric fibers.
(5) Design and synthesis of globular macromolecules capable of self assembling without conformational changes into soluble rod-like aggregates that can be stretched under shear into crystalline insoluble fibers.
(6) Use of water as the solvent for lyotropic nematic aggregates.
(7) Use of very low temperatures and pressures for preparation of high-strength/high-temperature fibers.
(8) Preparation of high performance biodegradable and digestible fibers.
(9) Utilization of enzymes for synthesis and degradation of fibers.
(10) Finally, we must be also be aware that the material presented in this article and the understanding of silk forming processes could not be achieved without the most recent advances in polymer science, bioengineering and molecular design.
(11) Man-made fiber technology based on the principles of natural silk formation would provide solution for several key problems of present man-made fiber technology such as:

- ecologically acceptable manufacturing,
- replacement of exotic or harmful solvents with water,
- biodegradability and
- energy consumption.

Also taking into account the recent advances in bioengineering, the presented fields should be a promising territory for long range fundamental research with well defined material and societal objectives.

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