Perspective

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Copying and Manipulating Nature: Innovation for Textile Materials†

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Abstract: This paper considers the potential impact of biological approaches such as bio-copying (biomimetics) and biomanipulating (e.g. genetic engineering) on future developments in the field of textiles and, in particular, fibres. If analytical tools for studying biological systems combined with those of materials science are further developed, and higher efficiency and reproducibility of genetic engineering technology can be achieved, the potential for the copying and manipulation of nature for textile innovations will be immense. The present state for both fields is described with examples such as touch and close fastener, structurally coloured fibres, the Lotus effect (for bio-copying), as well as herbicide tolerant cotton, insecticide resistant cotton (Bt cotton), cotton polyester bicomponent fibres, genetically engineered silkworm and silk protein, and spider fibres (for genetic engineering).

Keywords: Biomimetics, Genetic engineering, Natural fibres, Touch and close fastener, Structurally colored fibres, Lotus effect

Introduction

Nature and textiles have had a close relationship since time immemorial. Wool, silk, and cotton are among the oldest natural materials used by man. Natural fibres have, at present, a share of 46 % of world fibre consumption. It is forecast, however, that this figure will decrease to a global market share of 28 % by 2010[1]. Natural dyes, which have been used exclusively up to the beginning of the last century, are already completely replaced by synthetic products in the dyeing industry. However, in the long run, it might be wrong to draw the conclusion from these developments that "learning from and using of living systems" is outdated for the textile industry. Contemporary research has led to better understanding and important discoveries of complex principles that exist in nature. Because these discoveries are occuring during the same period of time as the development of the capability of materials science technology to fine tune man-made systems right down to the nanometre level, bio-copying can now be done at the nano-level. In addition, due to the rise of genetic engineering technology, natural fibres can now be modified without changing (which usually results in damaging) their highly prized basic properties, as normally happens in chemical modification. The outlook for bio-based fibres is therefore promising. This paper first discusses the copying of nature and then describes the use of genetic engineering for fibres and textiles in more detail. The achievements made will be described with examples.

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†Dedicated to Prof. Dr.-Ing. Dr. h.c. mult. H. Zahn on the occasion of his 85th birthday

Copying of Nature for Textiles

The copying of nature can be described with several different terms. Biomimetics means the studying of living systems with regard to imitating them for solving technological problems. Bionics describes various phenomena and functions which characterize biological systems with particular reference to electronics. In the field of fibres and textiles, the biological approach is particularly successful when bio-copying is applied to tailor-made synthetic polymers, including synthetic fibres. It is clear that chemistry stands to learn significantly from nature, and that chemistry and nature together can give rise to enormous synergistic advantages. Bio-copying can be used for all steps in the textile processing chain. This is demonstrated by the following examples.

Touch and Close Fasteners

The principle used for these fasteners is very well known because it is found in burrs.

The barb hooks which can be seen in Figure 1 can combine with every type of fabric. This is the basis for hook and loop fasteners. The principle for the anchoring of the barb hooks to a fabric with loops on its surface is demonstrated in Figure 2.

Another type of these fasteners is based on mushroom-shaped protuberances which can penetrate the entangled filaments and form strong links through mechanical interlocking. Figure 3 shows this type of fastener.

These principles of combining fibres, the most well-known application being in sport shoes, are used in an increasingly diverse range of forms and applications in non wovens as well as woven and knitted fabrics made from thermoplastic fibres (polypropylene, polyester and nylons). Hook and loop fasteners can be produced by established textile manufacturing operations, like calendering, heat-setting, cutting, shearing, and singeing.

Figure 1. Microphoto of a burr with its typical barb hooks. (Reproduced by courtesy of O. Meckes and N. Ottawa and with the permission of eye of science).

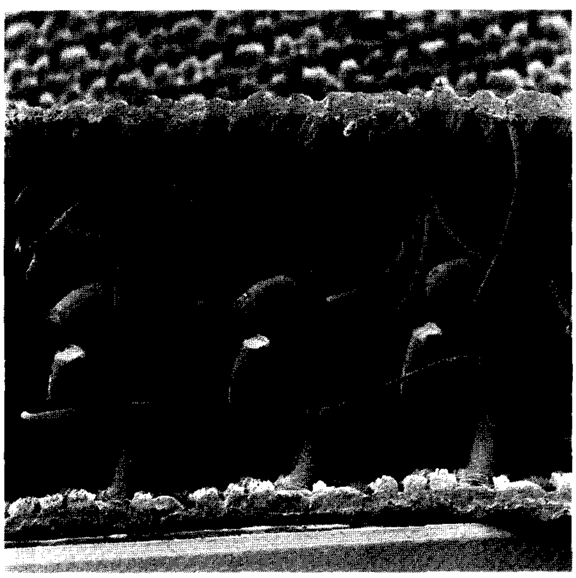


Figure 2. Microphoto of a closed hook and loop fastener. (Reproduced by courtesy of O. Meckes and N. Ottawa and with the permission of eye of science).

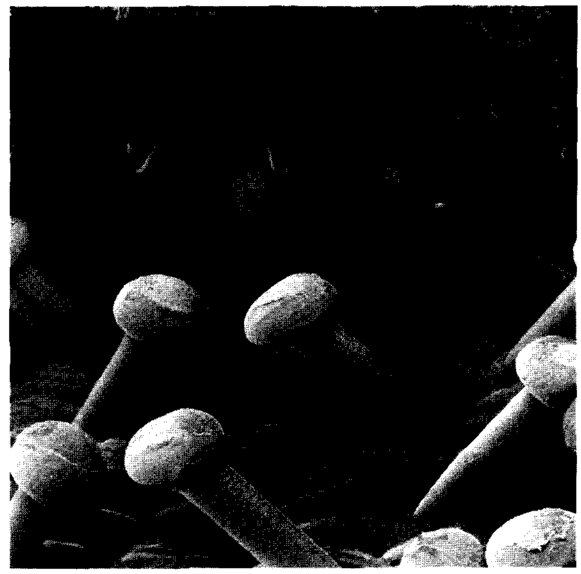


Figure 3. Microphoto of a touch and close fastener with mushroom -shaped protuberances. (Reproduced by courtesy of O. Meckes and N. Ottawa and with the permission of eye of science).

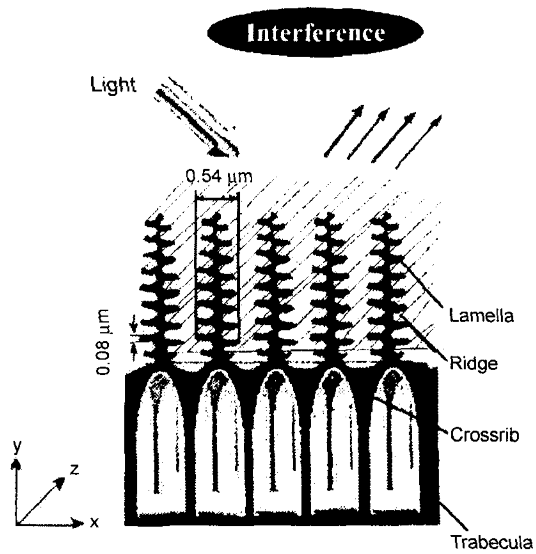


Figure 4. Sectional structure of a *Morpho sulkowskyi* scale and colour formation. (From ref. 2; reproduced by permission of Deutscher Fachverlag, Frankfurt).

Structurally Coloured Fibres

Certain kinds of insects (bugs and butterflies being studied in particular, e.g. *Morpho sulkowskyi*) show characteristic bright and clear colours, and some species show colour change with observation angle ("flopping colours"). This coloration is not due to the presence of colorants but to the interference of the reflected light caused by the characteristic periodical lamella structure in their cover and basic scale. A simplified model as shown in Figure 4 demonstrates how the colour is formed.

The same type of coloration can be observed with thin films of oil on a water surface. This "natural mechanism" for the formation of colored light has recently been transferred to synthetic fibres by the co-operation of three Japanese companies, one of which is a fibre producer[2]. By designing a multilayer structure (...polyester/nylon/polyester/nylon...) which is controlled strictly to give a certain calculated layer

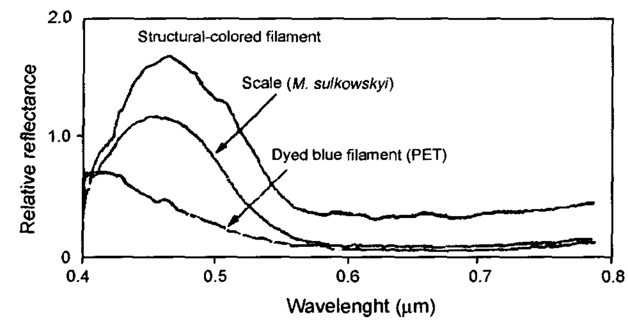


Figure 5. Reflective spectra of some samples colored in different ways. (From ref. 2; reproduced with permission of Deutscher Fachverlag, Frankfurt).

thickness, colored filaments were successfully obtained. These are comparable in their reflectance curve to dyed blue fibres as well as blue butterfly wings as is shown in Figure 5.

These so called "Butterfly fibres" or "Morphotex fibres" show violet, blue, green, and red colours with a pure and metallic tone. Flopping occurs from violet to blue, and green to red. If these newly developed fibres are successfully introduced into the market, there will be no longer any need for the usual dyeing process. This means there would be no need for dyestuffs, pigments, and auxiliaries at all. Toxicological and ecological aspects related to dyes and dyeing would no longer play any role in the industry. In addition, this type of coloration has, in contrast to conventional dyes, an unlimited lightfastness, which is highly desirable for many applications such as in automotive textiles.

Lotus Effect for Self Cleaning Textile Surfaces

A recent example of the copying of nature in textile finishing is the use of the "Lotus Effect" for soil repellent finishing. The basis for this effect is the observation that all primary parts of plants, except roots, are covered by a hydrophobic cuticle which provides the interface between plants and their environment. Scanning electron microscopy studies in combination with soiling experiments have revealed that water repellent plants with a microscopically rough cuticle structure (rough surface) show a strongly reduced surface adhesion to soil. Due to the decreased contact area between the plant surface and the soil and the easy rolling off of water droplets, soil can be easily transported together with the water and therefore removed from the surface. The particles adhere to the water droplets when they roll off. Figure 6 shows the different situations for smooth and rough surfaces.

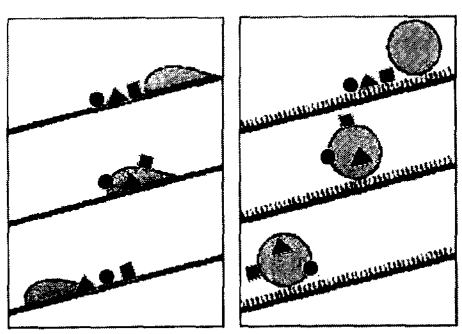


Figure 6. On smooth surfaces, dirt particles (black) are redistributed (left). On rough surfaces, the particles adhere to the droplets (grey) and are removed when the droplets roll off (right) (From ref. 3; reproduced by courtesy of W. Barthlott and C. Neinhuis and with the permission of Springer Verlag, Heidelberg).

This "self cleaning" mechanism is the basis for the purity of the lotus plant[3]. For this reason, this mechanism of decontamination is called Lotus Effect. This approach allows the substitution of sometimes environmentally harmful soil release agents used in textiles[4]. Since this roughness can be formed right down to nanometre dimensions, this type of surface modification is also called nano finish.

Genetic Manipulation of and for Bio-based Fibres

With well-understood procedures and techniques in Genetic Engineering or Genetic Manipulation, we are now capable of combining deoxyribonucleic acids (DNAs) from widely different organisms *in vitro*, i.e. from species which would not naturally crossbreed. The definition is sometimes broader and also includes direct modifications of DNA such as chemical modification. Since natural fibres are based on biopolymers which are also important in medicine, food, and agriculture, these fibres are now the subject of interest for molecular biology and genetic engineering. Two directions of research can be observed. a) The highly specific modification of natural fibres to introduce new properties. In this approach of genetic engineering, a breakthrough has already taken place and the resulting products have been marketed in large quantities. b) The manufacture of scarcely-available fibre forming biopolymers on an industrial scale. A practical realization of this approach, however, is still pending. Examples for both genetic engineering approaches are given below.

Bt Cotton and Herbicide Tolerant Cotton

Genetic engineering is already applied on a large scale for

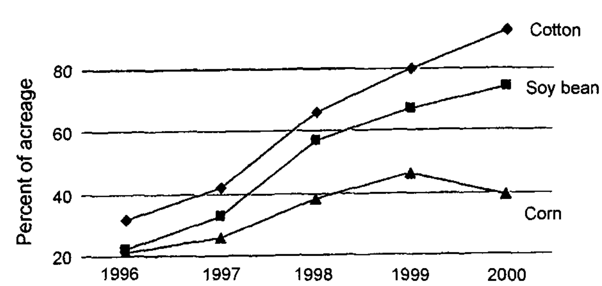


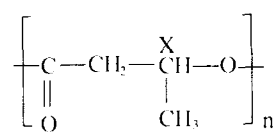
Figure 7. US adoption of transgenic crops[6].

the modification of cotton. In 2000, already 16 % of the global area for cotton cultivation worldwide is planted with genetically modified cotton[5]. The US is the frontrunner in this field. As shown in Figure 7, the production of genetically modified (transgenic) cotton in the U.S.A. has increased considerably during the last 15 years, with cotton being the most prominent compared to other crops[6].

The People's Republic of China is also fully focusing on insect-resistant cotton varieties obtained by genetic modification. The modification is in principle quite simple, and the mechanism involved has been known for quite some time[7]. The genetic modification for Bt Cotton can be taken as an example. A piece of DNA from *Bacillus thuringiensis* (Bt), a common soil bacterium, is introduced into the cotton cell. This DNA controls the formation in the cotton cell of a protein that is toxic for certain insects (Bt toxin). When a bollworm, one of the most prominent pests for cotton, eats the cotton, the toxic protein enters the intestine (the gut) of the insect where it causes interruption of digestion. This mechanism eliminates the bollworm before it can cause significant damage. Far less pesticides have to be applied to the fields planted with cotton modified in this manner. This is a great benefit not only because many pesticides are harmful to humans and the environment, but also because they are expensive. A problem is, however, that there are other pests besides the bollworm which are not fully protected against by this specific modification. Besides insect-resistant cotton, there are also herbicide-tolerant varieties and varieties combining these two traits. The herbicide-tolerant varieties were developed through the transfer of genes, allowing the plant to detoxify the active herbicide molecules (e.g. glyphosate or bromoxynil). Although genetically modified (transgenic) cotton shows many benefits, there are still some open questions which can only be answered when the long-term impact of these varieties is followed up. These questions relate to health risks (for cotton by-products, e.g. seed oil), to the uncontrolled dissemination of the transgene, to the development of resistance by the target insects, and to the ecological impact of Bt toxins on various other organisms. In view of these risks, the plantation of genetically modified cotton is not authorized in the European Union, but field trials have already been conducted in Spain, Greece, and France[8]. Herbicide tolerant and Bt cotton are described here in more detail to illustrate the extent to which genetic engineering has penetrated the fibre area regardless of many unanswered questions and risks. The modification of transgenic cotton today, as in the case of herbicide tolerant and Bt cotton, however, aims at improving on productivity rather than on innovation for textile materials. Further improvement in cotton productivity can be achieved when the genes for cell differentiation in cotton have been identified. With genetic manipulation of these genes, the process of differentiation can be intervened. As it is known that fibres are differentiated from seed-coat teguments cells, this approach can possibly increase the number of fibres per unit of seed coat surface.

Cotton with New or Improved Service Properties

Although a breakthrough with regard to practical realization beyond the laboratory scale has not yet been registered, improvement of the traditional properties of cotton fibre such as strength and length, as well as coloration, absorbance, and thermal properties has also been a target for genetic engineering[9]. Most work has focused on the genetic modification approach developed, but the applicable outcomes in terms of improving fibre property or quality have been indefinite. There has been certain unpublished research involving the expression of the genes (i.e. the production of the proteins from the genes) in melanin and indigo biosynthetic pathways in cotton, with the purpose of producing naturally black and blue fibres respectively[10]. Other unpublished work in China concerns the transfer of rabbit keratin gene into cotton to give "mohair-type" fibres[10]. Most spectacular of all this work was the announcement that a bicomponent fibre consisting of cotton and aliphatic polyester could be obtained by introducing the bacterial genes responsible for the formation of polyester into cotton[11]. More specifically, the gene encoding the formation of two enzymes necessary for the formation of poly(β-D-hydroxybutyrate) (PHB) can be transferred into cotton by particle bombardment. Since such a transgenic fibre has a higher heat capacity and a lower thermal conductivity, it exhibits better insulating properties than natural cotton.



Poly(β-D-hydroxybutyrate)

As has already been remarked in the previous chapter, a better understanding of the role of various genes in cotton fibre development may be the clue to achieving new properties and better quality. Once these genes are identified, their genetic manipulation could lead to the desired effects. Therefore, much research work is now being actively pursued on the molecular genetics of cotton fibre development[12]. Among these studies, Li *et al.* reported that the reduction of the cotton actin gene expression by means of genetic manipulation caused a dramatic reduction in fibre cell elongation[13]. Li *et al.* reported that the overexpression (i.e. the overproduction of the protein produced from the cloned gene in the cells) of a cotton beta-tubulin gene in yeast led to severe changes in cell morphology[14]. This same group of research also reported that the expression of a cotton profilin gene in yeast or in tobacco led to an increased cell length[15].

Genetically Engineered Silk Fibres

Another highly promising genetic manipulation for bio-based fibres is the genetic modification of silkworm (*Bombyx mori*) for new silk protein and silk fibres. Although the introduction of foreign genes (transgenesis) into silkworm is generally not efficient and reproducible at this time, and the screening of the transgenic silkworm is time-consuming, progress in this area is now gaining momentum. Many groups of researchers have recently been successful in developing gene transfer systems for silkworm which are efficient, easy for screening, and allow stable-inheritance of the transferred gene[16-22]. One of these approaches was the infection of silkworm larvae with a genetically engineered insect virus[16-18]. Another approach is to use a mobile genetic element called transposon as a vector to construct the recombinant DNA, which would then be injected into the silkworm eggs [19,20]. Another group transferred the recombinant DNA into the silkworm eggs directly by use of electrical voltage difference, a method called electroporation[21,22]. In most of these studies, a gene for green fluorescent protein (GFP) was used as a selection marker, which allowed an easy and straightforward way of screening for the transgenic silkworm. The transferred genes were found to integrate into the silkworm genome and transmitted through various generations. In some reports, the green fluorescent protein was found to be synthesized in the silkworm tissue, especially in the posterior silk gland, and was spun into the cocoon layer.

The powerful tool of genetic engineering, along with the reliable systems for transgenesis in silkworm as mentioned above, has opened the gate for engineering silkworm and, consequently, silk proteins for various desirable properties. Virus-resistant silkworm could be created which will be of great economic impact for sericulture. Silk composed of other foreign proteins such as those from spiders and silk with better physicochemical properties far beyond those obtained through polymer chemistry techniques can also be achieved. The silkworm itself can be engineered to serve as a machine for large-scale production of other foreign proteins because of its nature of prolonged production of protein. Finally, since silk protein fibroin has been used widely for bio-related applications and medical applications, mainly due to its biocompatibility with human tissue, one can engineer it to make bio-materials with new properties suitable for diverse applications[23]. One example is the synthesis of silk-elastinlike protein block copolymers which were pH- and temperature-sensitive by using genetic engineering technique[24]. This proved to have properties useful for the application of controlled gene delivery[25].

In addition to silk, wool, as an even more important protein-based fibre, has been successfully modified by genetic engineering. The results will not be discussed here because they have been reviewed elsewhere in full detail from the textiles point of view[26].

Spider Fibre

There are numerous spiders which form different types of

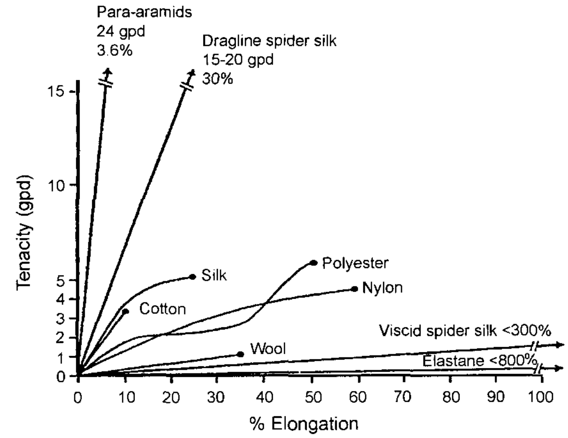


Figure 8. Tensile properties of spider thread compared to other fibres. (From ref. 27; reproduced by permission of Deutscher Fachverlag, Frankfurt).

Table 1. Elasticity modulus, viscosity modulus, and relaxation time of the frame thread compared with other fibres according to the calculations using the Poynting-Thomson model; PA 6: Polyamide 6, PTTA: Poly (p-phenylene terephthalamide), Kevlar-type[28].

	Frame silk (*Nephila madag.*)	PA 6	PPTA
Elasticity modulus E' (N/mm^2)	5.780	1.519	12.293
Viscosity modulus η' ($s \cdot kN/mm^2$)	3.451	363	5.660
Relaxation time $\tau = \eta'/E'$ (s)	597	239	460

protein fibres, some of which show extreme performance in terms of mechanical properties. This is shown in Figure 8 where the stress-strain curves of spider fibres are compared with those of other fibres[27].

The most outstanding properties are found with the dragline thread and the spoke or radial web threads of some giant spiders such as *Nephila madagascariensis* and *Nephila clavipes*. These fibres combine the advantages of a protein structure, including hydrophilic properties, biodegradability, biocompatibility, with high strength and high modulus, comparable to some synthetic high performance fibres but with an extremely high extension of break (with a value of 30 %). In addition, these fibres show a particularly high energy dissipation ability. The viscid spider threads form the core fibres of the capture spiral. These threads show an outstanding elongation at break, comparable to elastomeric synthetic fibres. The frame threads, not shown in the diagram (from *Nephila madagascariensis*), show an initial modulus with a value between those of para-aramids (Kevlar-type) and nylon 6. Moreover, within the low elongation range, the frame thread has a significantly higher strength level than that of nylon 6. For characterization of the energy dissipation ability, the viscoelasic properties of the fibres are of particular interest. Heinemann *et al.*[28] combined stress and relaxation experiments with subsequent evaluation of the results on the basis of a Poynting-Thomson Model for this purpose. By using this model, the three factors for the elongation behaviour of the spider silk frame thread, together with the values for some other fibres shown in Table 1 could be determined.

As can be seen, the relaxation time can act as an indicator for the relaxation behaviour, and thus for the viscoelasticity. The relaxation time of the frame thread is considerably higher than that of nylon 6, with its value between those of para-armid and *Bombyx mori* silk. The mechanism for fibre formation and the reason for outstanding properties of the spider fibres obtained from biological spinning process has not yet been discovered. However, plausible explanations can be given for the following causal relationships: chemical structure of the protein, composition of the biological spinning solution, technology of the spinning process, structure and properties of the native fibre. These relationships were described by Vollrath and Knight[29]. The spinning solution in the spider is liquid crystalline. Its protein concentration increases during its transport in the spider's body to a high value, and then undergoes specific protein folding. This process involves an unusual internal drawdown within the spider's spinneret which does not occur in industrial fibre processing. The subsequent drawing outside the spider, however, corresponds to the drawing process known in industry. A patent has already been filed for a very sophisticated spinneret, based on these ideas[30]. The property profiles of these fibres are so special that academic and industrial research groups all over the world are now actively working on these fibres. There is, however, a problem that these fibres are not as easily available as other natural fibres. Spider farming is difficult to put into practice. A solution for this problem would be to transfer the spider genes coding for spider thread proteins into other organisms which would in turn be able to produce these proteins. After isolation of the proteins, man-made fibres could be made by wet spinning. Two approaches have been studied and published. A "synthetic" DNA coding for dragline protein of *Nephila clavipes* was prepared, inserted, and expressed successfully in the bacteria *Escherichia coli* and the yeast *Pichia pastoris*. However, the overexpression of the larger protein segments was not achieved[31]. An alternative method would be the use of transgenic plants such as tobacco and potato for expression of this synthetic DNA[32].

Another approach[33] consists of the isolation of the thread gene from the spider, its introduction into a goat, and the production of spider proteins similar to the original ones. The technology used relies on the anatomical similarities between the fibre producing gland of the spider and the goat mammary glands. This approach has proven to be successful. Threads with relatively good properties, though not comparable to that of the native one, could be obtained from aqueous medium for the first time. These threads were drawn by hand. Their properties may be greatly improved if the hand drawing is replaced by a mechanical drawing processes used in industry. The yield of the protein, however, was very low since there was a big loss during the purification and the concentration processes of the protein.

Conclusions

Nature continues to be a resource for further development in the fibre and textile field. Because the analytical tools and facilities for studying living systems will continue to be improved, it can be predicted that many more naturally occuring phenomena, mechanisms, complex systems etc. will be discovered and elucidated. When novel practical applications can be envisaged, these too can be transferred to the fibre and textile field by bio-copying. Genetic engineering has already shown its potential with the commercialization of transgenic cotton. The success of any genetic modification, however, has until now depended very much on individuals skills. When these techniques gain improved reproducibility, natural fibres and fibre forming polymers will progress, overthrowing all current forecasts. A key prerequisite for copying and manipulating living systems is a rich choice in biological species. Bio-diversity will therefore be one of the important factors influencing which regions of the world will gain leadership in copying and manipulating nature in the fibre and textiles field.

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