Biomimicry as a route to new materials: what kinds of lessons are useful?

Emily J Reed, Lisa Klumb, Maxwell Koobatian and Christopher Viney

*Phil. Trans. R. Soc. A* 2009 **367**, 1571-1585

**References**

This article cites 36 articles, 3 of which can be accessed free
http://rsta.royalsocietypublishing.org/content/367/1893/1571.full.html#ref-list-1

**Rapid response**

Respond to this article
http://rsta.royalsocietypublishing.org/letters/submit/roypta;367/1893/1571

**Subject collections**

Articles on similar topics can be found in the following collections

- materials science (134 articles)
- biophysics (311 articles)

**Email alerting service**

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](http://rsta.royalsocietypublishing.org/subscriptions)

To subscribe to *Phil. Trans. R. Soc. A* go to:
http://rsta.royalsocietypublishing.org/subscriptions

This journal is © 2009 The Royal Society
Biomimicry as a route to new materials: what kinds of lessons are useful?

BY EMILY J. REED 1, LISA KLUMB 3,†, MAXWELL KOOBATIAN 2 AND CHRISTOPHER VINEY 1,*

1 School of Engineering, and 2 School of Natural Sciences, University of California at Merced, PO Box 2039, Merced, CA 95344, USA
3 Center for Bioengineering, University of Washington, Seattle, WA 98195, USA

We consider the attributes of a successful engineered material, acknowledging the contributions of composition and processing to properties and performance. We recognize the potential for relevant lessons to be learned from nature, at the same time conceding both the limitations of such lessons and our need to be selective. We then give some detailed attention to the molecular biomimicry of filamentous phage, the process biomimicry of silk and the structure biomimicry of hippopotamus ‘sweat’, in each case noting that the type of lesson now being learned is not the same as the potential lesson that originally motivated the study.

Keywords: biomimicry; filamentous phage; hippopotamus; liquid crystal; silk

1. Biomimicry and engineered materials

(a) Successful engineered materials

Biomimicry can be a powerful concept and a practical tool in the development of new materials. If we are confident in identifying the attributes of a successful engineering material, we can also recognize when lessons from nature are relevant and valuable.

A successful engineering material must, of course, exhibit one or more physical (structural, mechanical, electrical, thermal and magnetic) or chemical (adhesive, reactive, catalytic and non-reactive) properties that are optimized for a particular application. The idea that a single material can be multifunctional, i.e. exhibit more than just one optimized property, has become more tractable as engineers have become increasingly adept at using structure at different length scales in a material to control the different properties. This realization in itself has been reinforced by several examples from nature (Jeronimidis 2000), including the hierarchical structure of collagen. It is fitting to consider production cost, required service life, maintenance and repair costs and end-of-use recyclability as additional critical properties.

* Author for correspondence (cviney@ucmerced.edu).
† Present address: Amgen, Inc., MS 28-4-A, One Amgen Center Drive, Thousand Oaks, CA 91320, USA.

One contribution of 9 to a Theme Issue ‘Biomimetics I: functional biosurfaces’.
Achieving the desired set of properties in a successful engineering material requires the selection of appropriate ingredients (composition), along with the choice of an appropriate process to ensure that the ingredients form the right microconstituents (phases), with the right morphology, over the right length scales (Callister 2007).

From a materials engineering point of view, biomimicry adopts the premise that natural materials (and processes that lead to them, and devices that depend on them) have evolved over a very long period of time, under conditions that favour the efficient use of available resources and that, by definition, are biocompatible. If a natural material—or, by extension, a natural device that depends inseparably on material properties—does a better job than an existing synthetic counterpart, then biomimicry of that material should be considered. In this context, ‘does a better job’ includes having enhanced properties, using less material, or being cheaper or more robust or more environmentally friendly, or simply being less obtrusive. There is also an implication that none of the other desirable aspects of the existing engineered material are significantly compromised in the natural product being considered as an object for biomimicry.

\( (b) \) Materials produced by natural processes

Natural materials (in the present context, referring to materials produced metabolically by living organisms) have many impressive credentials. However, natural materials are not intrinsically superior to artificial ones. Nature and technology serve different goals, usually under very different constraints (Vogel 2003). (We will leave aside any philosophical debate predicated on the fact that humans are themselves an integral part of nature, and that human technology is therefore just another manifestation of what nature can achieve.)

In nature, the building blocks of materials structure are synthesized from relatively few types of atom. Most of the periodic table does not feature in the ingredients of natural materials, and, as far as we know, natural organisms do not make metallic materials. Nature’s processing strategies operate close to ambient temperature, and under near-equilibrium conditions. Consequently, few of nature’s materials are made quickly enough or on a scale large enough to be of interest to materials engineers (although, taking a broader view, we must acknowledge wood, plant and animal fibres and natural oils as valuable raw commodities, and no engineer can survive without food).

The ubiquitous presence of organic matter in natural materials precludes the use of these materials at high temperatures. At the same time, the close association between natural materials and living tissue allows natural materials to be regrown or repaired or replenished. The size of device for which nature optimizes its materials is therefore limited by the logistics of delivering reagents to the sites of growth and repair, and natural materials are generally poor role models for long-term maintenance-free durability.

\( (c) \) Selective biomimicry

‘Biomimicry’ (denoting a design process) and ‘biomimetics’ (denoting a field of study in which that design process is applied) are perhaps unfortunate terms in that they engender the impression that nature is being copied—literally mimicked—without giving thought to the value or limitations or consequences...
of such copying. The suitability of various bio-buzzwords has been discussed previously (Viney 1993), as have the pitfalls of assuming that nature’s designs are always the best (Vogel 2003). The apparent practice among some researchers of over-interpreting tenuous connections between imitating nature and creating startling new materials has been questioned eloquently (Roy 1991).

It can be instructive, however, to study nature’s materials, processes and devices, and so identify situations where nature offers useful solutions to properly focused questions that may or may not have been posed first by technology. In other words, nature can open our eyes to possibilities (Viney 2001), much as Leonardo da Vinci’s observations of birds in flight contributed significantly to the belief that people could also conquer the skies. Of course, the path to our present-day success in aviation (and the ability to fly heavier loads much faster than birds can) did not depend on flying machines that work by flapping their wings up and down, but on our recognizing that a wing with variable curvature is the key to balancing lift and drag over a range of speeds. Similarly, successful biomimetic materials are those where ‘what if’ questions are informed by knowledge of biology, and the answers are open to refinement from any pertinent field of expertise.

The extent of the symbiosis between technology and biology has been investigated quantitatively (Vincent et al. 2006), revealing that the present technology solves problems largely by manipulating the use of energy, while biology relies heavily on structure and information storage. This analysis is useful because it helps us to focus on which aspects of the natural world (and which aspects of its relevant processes) might be most usefully transferred to technology via the judicious practice of biomimicry.

2. Case study 1: filamentous phage as an example of molecular biomimicry

(a) Why filamentous phage?

Filamentous phage is of interest in biomimetic materials engineering because it performs robustly as a promoter of liquid crystalline phase formation, and hence can facilitate the ‘bottom-up’ self-assembly of complex materials. A geometrically anisotropic mesogen is ensured by the juxtaposition of a DNA core and a surrounding self-assembled protein capsid, the latter consisting of a large number of copies (approx. 2800 in the case of bacteriophage M13; Makowski 1994) of a coat protein. The techniques of genetic engineering can be used to modify the DNA core so that each protein molecule in its cylindrical coat displays a consistently altered peptide sequence at the outer surface. In this way, phage particles with a tailored charge distribution and hence functionality (i.e. ability to bind to other molecules or small particles) can be created. The potential variety of functionalities is extensive, limited only by the resourcefulness of the molecular biologist who controls which novel foreign peptide is displayed on the surface of the modified phage.

If the tendency to self-assemble is sufficiently strong, the phage can serve as a host that guides the self-assembly of complex structures and templates that are useful in nanofabrication (Flynn et al. 2003; Merzlyak & Lee 2006). Examples
include M13–lipid complexes (Yang et al. 2004), ordered M13–ZnS nanocrystal films (Lee et al. 2002), M13-templated nanowires (Mao et al. 2003) and even scaffolds that promote the patterned alignment and growth of cells (Rong et al. 2008).

In these instances, the biomimetic aspect of the phage-containing materials lies in the structure of the mesogenic moiety (i.e. the phage) that promotes their self-assembly, rather than in the resultant material structure. The term ‘molecular biomimetics’ (Sarikaya et al. 2003) is an appropriate descriptor of this type of biomimicry. The processes by which multiple copies of a particular wild-type or modified phage are generated are presently too complex to emulate by in vitro chemistry, and one has to rely on insertion of the phage into a bacterial host to accomplish the synthesis of large amounts of phage. In other words, the processing steps are bio-dependent rather than biomimetic.

Another aspect of molecular biomimicry using phage display has been demonstrated in the form of phage that was decorated with protein capable of selective binding to trinitrotoluene and 2,4-dinitrotoluene (Jaworski et al. 2008). Thin layers of the modified phage mimic receptors in the olfactory system of animals such as bloodhounds, with respect to both selectivity and sensitivity. It can be anticipated (Jaworski et al. 2008) that a similar approach will be useful in the production of substrates to detect other volatile organic compounds, including pesticides, food aromas and disease markers.

(b) Liquid crystalline phases of filamentous phage

Previous authors have described the formation of nematic (Lee et al. 2003), cholesteric (Lee et al. 2002) and smectic (Lee et al. 2003) phases by M13 or related fusion phagemids at different concentrations. In our own work, we have explored whether the type of self-assembled phase formed is sensitive to changes in the route (increasing or decreasing the amount of water present) by which a particular phage concentration is obtained.

The phagemid system that we used is based upon the M13 filamentous bacteriophage. The control phage particle is a pBluescript (Stratagene, La Jolla, CA) phagemid of approximately 3000 nucleotide bases long, encapsulated with wild-type M13 coat proteins. The fusion phagemid is 3100 bases long, and encodes for a 62-residue protein L IgG-binding domain fused to the N-terminus of the gene VIII protein (Gu et al. 1995). Both types of virus particles are roughly half as long as the wild-type M13 filamentous bacteriophage, calculated using the ratio of 2.3 bases for one gene VIII protein, with the same diameter as wild-type M13 (65 Å). The pBluescript virus particle is roughly 5000 Å long, assuming 3.8 Å between gene VIII proteins (Berkowitz & Day 1976) and the protein L fusion phage is 5300 Å, assuming that the insert has not altered the base-to-protein ratio or the distance between gene VIII proteins.

The two filamentous bacteriophage types—pBluescript (Stratagene, La Jolla, CA) as the control, and the protein L construct—were received as phagemid particles. These, along with XL1-Blue cells (Stratagene; an F+ strain of Escherichia coli used to propagate the phage) were all generously donated by the laboratory of David Baker, Department of Biochemistry, University of Washington, Seattle, WA. Construction of the protein L phagemid has been described elsewhere (Gu et al. 1995). The helper phage used was M13KO7
(Biorad), at a concentration of $2.4 \times 10^{11}$ pfu ml$^{-1}$ (‘pfu’ denotes plaque forming units). Both phagemid vectors confer ampicillin resistance to their hosts, and M13KO7 confers kanamycin resistance.

The methods used for the production and purification of phagemid particles have been described in detail elsewhere (Smith & Scott 1993; Gu et al. 1995). The production of phagemid particles consisted of inoculating 750 ml of LB growth media with 1 per cent by volume of XL1-Blue cells previously infected with the desired phagemid, in the presence of ampicillin (100 µg ml$^{-1}$) to select for those bacteria harbouring the phagemid. To this mixture was added $1.8 \times 10^{10}$ pfu of the helper phage, M13KO7, followed by slow shaking for 1 hour at 37°C to allow for the binding and infection of the cells with the helper phage. Kanamycin was added (70 µg ml$^{-1}$) to select for those phage harbouring both the M13KO7 and the phagemid, and the mixture was shaken vigorously for 14–18 hours at 37°C. The cells were then removed by centrifugation, and the phage-containing supernatant was subjected to two rounds of phage particle precipitation with polyethylene glycol/NaCl solution (2.5%/0.5 M). Following the second polyethylene glycol precipitation and removal of all supernatant from the phagemid particle pellet, the phagemid particles were separated from cell debris and residual polyethylene glycol via a CsCl gradient, established using ultracentrifugation in a 31 per cent w/w CsCl solution. After pulling the phagemid particle containing band from the CsCl gradient, the particles were washed and pelleted via ultracentrifugation twice with ultrapure water (NANOpure, Barnstead). This procedure resulted in a gelled pellet of phage particles. The approximate concentration of the solid was 27 per cent by weight, estimated from weight loss measurements when the pelleted material was allowed to dry.

Samples for transmitted polarized light microscopy were prepared by confining small amounts of the pelleted material between a clean glass microscope slide and coverslip. A reproducible initial condition was imposed on the samples by subjecting them to shear; the coverslip was pressed down firmly and displaced parallel to the length of the slide at approximately 10 cm s$^{-1}$. This treatment generated a banded microstructure (figure 1a,b) that is typical of sheared nematic and cholesteric liquid crystals (Viney & Putnam 1995). The banded microstructure was observed both in the fluid material retained under the cover slide and in the ‘trail’ of dried material left on the slide in the wake of the moving coverslip.

On some sheared samples, a new coverslip was placed over the dried trail, with an edge lying along the edge of the glass slide. Then, with the slide held vertically, this side of the sample was immersed in approximately 1 mm deep water so that water would be drawn into the space between the slide and coverslip, rehydrating the dried phage. The banded microstructures in these samples relaxed via a sequence of complex textures (figure 1c,d) into a finely textured herringbone or chevron pattern (figure 1e,f).

The fluid material under the cover slide used for shearing was either held at constant concentration by sealing the edges with vacuum grease, or it was allowed to dry slowly as water was lost by evaporation from the edges. In the former case, the banded microstructures relaxed over a period of several hours into a nematic schlieren texture characterized by disclinations with half-integral strength (figure 1g); additional relaxation over several days led to coarsening of the microstructure, with alignment persisting over larger distances as the
number of disclinations decreased (figure 1h). In samples that were allowed to dry slowly, the material reorganized itself into a complex cholesteric microstructure over a period of several days (figure 1i, j). The observations described above pertain to both of the M13 filamentous bacteriophage types that we studied, which is consistent with their liquid-crystalline phase formation being driven by similarly high phage length-to-width ratios, and similar contributions from intermolecular forces (Flory 1984).

The main point to emerge from these observations is that the detailed pattern of supramolecular self-assembly by filamentous phage does not just depend on concentration, but also on the kinetic route by which the concentration is achieved. In other words, the result of self-assembly depends on whether we start...
with a concentration below or above the target and on the rate of concentration change. The variety of potentially useful self-assembled patterns that can be achieved with a given type of phage is expanded by this realization, which is consistent with lyotropic phase formation being a nucleation-dependent process (McEwen et al. 2001).

3. Case study 2: silk as an example of process biomimicry

(a) Why silk?

All spiders, and several insect and myriapod species, depend on silk for one or more essential functions, such as prey capture, habitat construction and protection of their eggs (Viney 2000). Usually, the organism that stands to benefit from using the silk is also the producer of the silk, but an interesting exception is provided by adult weaver ants that use larval silk as a structural component of their nests (Dorow et al. 1990). Widespread attempts to copy the molecular order in, and mechanical properties of, natural silk fibre have been prompted by the observation of how this material is deployed in nature and from measurements of the average strength and stiffness in standard (short-duration) tensile tests.

Unfortunately, there are some significant differences between the properties typically required of a successful engineering material and the properties of natural silk. Structural engineering materials are usually expected to carry large loads reliably for long times, minimizing the need for repair or replacement. By contrast, natural silks, though load-bearing, are subjected to their maximum design load for only short periods of time (perhaps never, if, for example, a cocoon escapes the attention of predators). Spider dragline silk additionally is prone to supercontract in water (Work 1981), undergo stress relaxation (Bell et al. 2002) and exhibit significant creep (poor long-term load-bearing ability) (Smith et al. 2003) that is exacerbated by moisture (Viney & Bell 2004; Ritchie et al. 2005). Silkworm cocoon silk is also susceptible to creep and stress relaxation (Morrison et al. 2004; although moisture affects these time-dependent responses much less drastically than in the case of spider dragline; see results below). The tensile properties of both spider dragline (Pérez-Rigueiro et al. 2001) and silkworm cocoon silk (Pérez-Rigueiro et al. 1998) are poorly reproducible, so that these materials are unsuitable in critical applications where the ability to predict failure accurately is paramount.

At the same time that the limitations of silk as a load-bearing engineering material were being assessed, researchers became increasingly adept at producing silk and analogous materials in genetically modified hosts (Vendrely & Scheibel 2007). One feature of natural silk that has persisted in its appeal to biomimicry—regardless of the target properties—is the fact that silk fibres are spun from aqueous solution into water-insoluble material, accompanied by changes in the physical state (conformation), but not the chemical nature of the protein. This blueprint for environmentally friendly processing is based on the ability of water-soluble globular silk protein molecules to aggregate into a processable liquid crystalline fluid that promotes flow, in turn creating the conditions that promote elongation of the molecules and the local formation of water-insoluble crystalline domains (Viney 1997).
Similarly, artificial processing of aqueous silkworm fibroin solutions has resulted in material properties that mimic the behaviour of native silk (Jin & Kaplan 2003). Aqueous processing has also been used to produce prototypical silk lenses and diffraction gratings from solutions of silk fibroin; their transparency is ensured by controlling the crystallization of β sheets, and the products benefit from the mechanical properties and biodegradability of silk (Lawrence et al. 2008). Incorporation of useful components (such as enzymes) into silk networks can lead to many functionalizations of the silk as a substrate,

Figure 2. Creep curves for *N. clavipes* spider dragline silk in (a, b) air, (c, d) water and (e, f) ethanol. Time is plotted on a linear scale in frames (a), (c) and (e), and on a logarithmic scale in frames (b), (d) and (f). Applied stress is given as fraction of yield stress of dry spider silk in air.
creating bioactive surfaces with a multitude of possible biological applications that include the use of silk as a scaffolding on which to culture tissues such as bone (Sofia et al. 2001). Because silk is biodegradable, its use as a cell and tissue scaffold could be ideal as a material that would not require subsequent surgical removal. The biodegradability of silk fibroin scaffolds has been tested (Wang et al. 2008), with degradation times being controlled by the processing environments. Biodegradation also makes silk suitable for use as a controlled release drug delivery vector (Hardy et al. 2008).

Thus, although silk biomimicry originated in efforts to copy the structure of silk, and hence to emulate the perceived high performance mechanical properties of silk, the more useful lessons have thus far turned out to lie in the realm of materials processing.

(b) Post-process susceptibility to the processing solvent

The superior tensile properties of spider dragline silk compared with silkworm cocoon silk (as deduced from standard tensile tests conducted at constant strain rate over a time scale of several minutes) have tended to focus attention (i.e. a quest for successful structure and thence property biomimicry) on the former material. However, as noted above, dragline mechanical properties are affected
adversely by moisture, even though the spun fibres are water insoluble. The sensitivity to moisture is unsurprising if one notes that the amino acid sequences that confer water solubility to the silk protein prior to spinning are retained in the material after spinning. This inbuilt susceptibility to water represents a conundrum for engineers who want to adapt silk’s blueprint for environmentally friendly processing into a context for spinning high-performance, load-bearing fibres.

Tests performed on silk reeled directly from silkworms, rather than on fibre recovered from silkworm cocoons, have demonstrated that silkworm silk can, in fact, be made to exhibit tensile properties comparable with those of spider dragline (Shao & Vollrath 2002). Exposure to microwaves has been shown to virtually eliminate stress relaxation and creep in silkworm silk (Morrison et al. 2004), but was less effective as a treatment for spider dragline. Thus, it appears that silkworms may, in the end, be found to outdo spiders in producing more mimic-worthy silk properties. This prospect warrants investigation of the moisture sensitivity of silkworm silk creep.

As a point of departure, figure 2 shows the creep behaviour of Nephila clavipes spider dragline in air, water and ethanol. Frames (a), (c) and (e) collate data that have been published and dissected previously (Ritchie et al. 2005), while the corresponding frames (b), (d) and (f) facilitate interpretation by displaying time on a logarithmic scale. Indeed, the claim (Ritchie et al. 2005) that there are two regimes, and thus at least two mechanisms of creep, is more clearly justified by the rescaled plots; in some cases (e.g. dry spider dragline in air, subjected to a nominal stress equal to 0.4 times the yield strength; figure 2b), the existence of three creep regimes is apparent from these plots.

The broken vertical lines in frames (b), (d) and (f) of figure 2 mark the approximate onset time for the final, slowest stage of creep. This transition occurs when the silk polymer chains have exhausted their capacity to respond to the applied load by ‘easy’ mechanisms, such as increasing their local extension and alignment, so that further deformation is then constrained by chain entanglements and their effect on chain slip. Extension and alignment of chains can occur more readily (and so are exhausted sooner) if polymer–polymer hydrogen bonds are replaced by polymer–water contacts via exposure to a hydrating environment. Conversely, these two contributions to microstructural rearrangement are slowed (and so take longer to exhaust) if polymer–polymer contacts are increased by exposing the material to a dehydrating environment. Thus, the variable location of the transition marked by the vertical broken lines in figure 2 can serve as a straightforward indicator of how the creep of dragline silk is affected by moisture.

Samples of fibre that had been reeled from degummed Bombyx mori silkworm cocoons were subjected to creep tests in air and in water, using protocols that are identical to the ones (Ritchie et al. 2005) employed previously for spider dragline. The results are shown in figure 3, with time plotted on both linear and logarithmic scales. Unlike the spider dragline, silkworm cocoon silk does not exhibit significantly increased creep rates as a result of immersion in water, and there are no clearly identifiable transitions between regimes in which different creep mechanisms might dominate in either the dry or wet silk.

The absence of significant moisture sensitivity in the creep behaviour of silkworm silk is further cause to revisit at least this silk as a source of possible lessons in structure biomimicry. It is noteworthy that both spider dragline and
silkworm cocoon silk retain the amino acid sequences that rendered these materials water soluble prior to spinning, while only spider dragline is significantly water sensitive in its spun form. Thus, it would appear that the cocoon silk is able to ‘hide’ some of the hydrophilic components of its microstructure, perhaps by incorporating such components within regions that are sufficiently dense or outwardly hydrophobic to resist penetration by water. Microstructural characterization of both silks, at a level of detail that addresses this comparison, is needed.

4. Case study 3: hippopotamus ‘sweat’ as an example of structure biomimicry

(a) Why hippopotamus sweat?

Hippopotamus follow a daily routine that might be expected to expose the skin to potentially damaging doses of ultraviolet sunlight. The effectiveness of their red sweat (the common name for what, in this case, is really an oily secretion and not a watery excretion) as a barrier to ultraviolet radiation has been interpreted in terms of two UV-active chromophores that are present in the material (Saikawa et al. 2004). But the success of the sweat in its protective roles (as a sunscreen and also as an antiseptic (Eltringham 1999)), and its ability to spread so that it coats the skin easily and efficiently, must, in addition, depend on its physical structure. Studies of the physical structure of the secretion are therefore a necessary partner to analysis of its chemical constitution.

(b) Polymorphism of hippopotamus sweat

Physical characterization depends on samples that are compositionally as similar as possible to the native material. Our method of sample collection (at the Chaffee Zoo, Fresno, CA) involved the zoo staff admitting their hippopotamus into an (indoor) enclosure that was previously hosed clean with water. When the hippo stood or lay down in the enclosure, globules of the red secretion accumulated on the concrete floor. The sweat could be distinguished readily from other fluid material (e.g. faeces) by its colour, as well as by the fact that it did not attract the attention of the ever-present flies. After approximately 30 min, the animal was returned to its adjacent outdoor habitat. Secretion that had not been soiled or stepped on by the animal was retrieved from the floor with a pipette (Gilson Pipetman) and transferred to small, sealable plastic containers (Falcon polypropylene tubes). The containers were transported on ice to the laboratory, where they were stored in a refrigerator. Over a period of several weeks, the stored secretion slowly denatured, with suspended solids becoming evident to the unaided eye after approximately a month. Even then, however, there was no evidence of microbial (yeast, bacterial or fungal) contamination, consistent with the secretion acting as an effective antiseptic.

Samples for transmitted polarized light microscopy were prepared on the day of collection by confining material between a clean glass microscope slide and coverslip. The most commonly observed microstructure (figure 4a,b) consists of two types of coexisting fluid spherulitic (and thus liquid crystalline) structures, one of which is banded. The two types have opposite optical signs. Both types can nucleate from the optically isotropic background, and each can nucleate epitaxially...
on the other. Multilayer spherulites (figure 4c) occur frequently. We have not yet determined what causes non-banded material to nucleate banded material or banded material to nucleate non-banded material; however, successive enrichment and depletion of a microconstituent in the fluid ahead of the growing spherulite, due to that microconstituent having differing solubilities in the two spherulite structures, could drive the observed layering. The boundary between banded and non-banded material is diffuse, as demonstrated in figure 4d.

Figure 4. Transmitted polarized light microscopy images of hippopotamus ‘sweat’. Scale bars represent 10 μm in each frame. (a) Coexisting banded and non-banded liquid crystalline spherulites. (b) The same field of view as (a), with a full-wavelength (sensitive tint) plate inserted to demonstrate that the two types of spherulite have opposite optical signs. (c) Multilayer spherulite consisting of three zones (two zones of non-banded material flanking a banded zone). (d) Image (with a full-wavelength plate inserted) demonstrating a diffuse interface between banded and non-banded liquid crystalline spherulites. (e) Nematic schlieren texture. (f) Smectic fan texture (imaged with a full-wavelength plate inserted).
In the banded material, the spacing of bands is approximately 0.5 \( \mu \text{m} \), close to the resolution limit of conventional light microscopes. Such a fine microstructure will be effective at scattering light, conferring the sun-blocking properties on the material to complement the sun-screening ability imparted by the previously reported (Saikawa et al. 2004) chromophores. This realization in turn suggests the use of combined sunscreens and sunblocks to maximize the performance of thin layers of equivalent protective products for human use.

The observed polymorphism can thus benefit the hippopotamus in two ways. First, by incorporating effective light scattering entities in the microstructure, the hippo has more effective protection from damaging ultraviolet rays. Second, by incorporating the non-banded but microstructurally coarser liquid crystalline spherulites, the hippo gains a reduction in the viscosity of the sweat and thence an increase in the ability of the sweat to spread on the hippo’s surface.

Less commonly, the sweat formed microstructures more typical of nematic (figure 4e) or smectic (figure 4f) liquid crystals, coexisting with the spherulitic material. These polymorphs also combine effective light scattering (e.g. the scattering of light by nematics is higher by a factor of \( 10^6 \) compared with the scattering by conventional isotropic fluids (de Gennes & Prost 1993)) and reduced viscosity.

5. Conclusions

Biomimicry is both a mindset and a process that can lead to new or improved engineering materials. It is important to remember, however, that the designation ‘nature made’ does not confer intrinsic superiority.

Filamentous phage has a promising future in molecular biomimicry, where, in native or modified form, it can serve as a host that guides the alignment and self-assembly of other molecular species during nanofabrication. We have shown that the detailed pattern of supramolecular self-assembly by filamentous phage is sensitive to whether we start with a concentration below or above the target, thus expanding the variety of potentially useful self-assembled patterns that can be achieved with a given type of phage.

Although the biomimicry of spider dragline silk was originally motivated by the goal of engineered fibres that have superior strength, stiffness and toughness, it is apparent now that silkworm silk may be a better role model, given, among other considerations, its lower sensitivity to moisture. In the meantime, both types of silk have taught us that it is possible to process environmentally friendly (aqueous) solutions of protein into useful, water-insoluble material.

Hippopotamus sweat offers lessons on using liquid crystalline microstructures to introduce sun-blocking properties into thin layers of material, which also act as a sunscreen by virtue of their composition. Microstructural polymorphism provides a means of co-optimizing optical and flow properties of the sweat. Studies of the sweat also raise fundamental questions about the nucleation and coexistence of liquid crystalline spherulite polymorphs, which merit additional study.

Learning the science of how nature works may not always lead to lessons being transferred in the direction of practical engineering. However, there are always good possibilities that, as the scope of our knowledge continues to grow, today’s biological curiosity can become the object of tomorrow’s biomimicry.
The authors are grateful to Dr David Baker, Department of Biochemistry, University of Washington, Seattle, WA for donating materials. Useful technical assistance was provided by Joanne Ritchie and Christopher Smith (regarding silkworm silk) and Amber Zielinski (regarding hippopotamus sweat). The Chaffee Zoo, Fresno, CA kindly facilitated collection of the hippo sweat. Funding for the sweat study was provided by Unilever.

References


*Phil. Trans. R. Soc. A* (2009)


