

SILKS AND THEIR COMPOSITES

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ABSTRACT

Silk polymers have evolved as key structural components in a wide range of animal constructions. Examination of both silk fibres and silk structures, be they gossamer webs or paper-like cocoons, reveals intriguing insights into Nature's way of making materials and composites of considerable potential for novel insights with practical implications.

INTRODUCTION

Silks make not only interesting natural materials but also, in the context of their use by the animals that produce them, fascinating natural composites. Importantly, the material properties of a silk depend not only on the chemistry and subsequent folding pattern of the silk protein themselves but also on the hierarchical structure of the poly-protein fibre. Both, in turn, depend to a large extent on the conditions under which a fibre has been spun and thus depend on the animal's spinning behaviour. Not surprisingly, this gives the animal a high degree of flexibility in which to use its materials. And, if the materials (and typically silks are multi-faceted) are integrated into structures, then those too can have a range of ultimate properties, depending on the animal's building behaviour. As both materials and structures have evolved over hundreds of millions of years, much can be gleaned and learned concerning highly adapted and often optimized structure-property-function relationships on the material level as well as on the composite level.

Individual silk fibres can range in diameter from 20 to 7000 nm depending on species, animal size, silk type and spinning conditions. The hierarchical structure of a silk fibre can range from very simple to complex i.e. a singular

filament consisting of its molecular chains folded into regions with differing degrees of order to, respectively, bundles of filaments aggregated and layered into fibre-ropes and covered with coatings of specialist compounds [1].

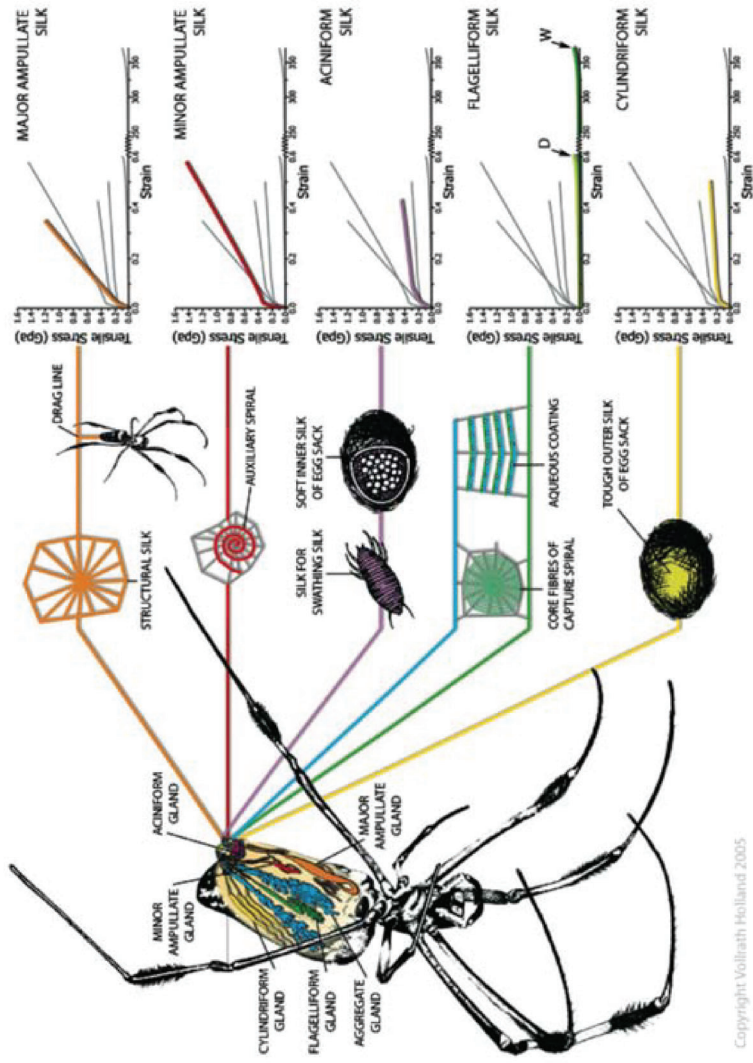
Presented here are two very different silk fibre and composite types: the many silks and light-weight webs of spiders and the singular silk and solid cocoon of lepidopteran “silkworm” larvae.

SPIDER WEBS AND SILKS

The spider’s orb web (which is an excellent example for a highly advanced web structure) incorporates silks of different chemical compositions and with different mechanical properties, connected into a polar network that has both firm and soft sections. The firm sections, the radii, transmit the vibrations that signal the presence of prey; they also form pathways on which the spider traverses its web. Moreover, the radii support the capture spiral, which is viscous, sticky and extraordinarily elastic. The softness prevents the capture spiral from interfering with the vibration transfer along the radii, which would be dampened by a tightly strung connecting spiral. In addition, its very softness is necessary to arrest the insect’s flight without catapulting it back out, trampoline-fashion, and to prevent purchase for the insect once caught struggling to escape.

All spiders produce more than one kind of silk with the female of the common garden spider having at least seven different kinds, each with its own production system consisting of gland, storage sac, duct, valve and spigot (Figure 1). The glands are hidden deep inside the spider’s abdomen but the spigots open on nozzles embedded atop highly mobile extremities, the spinnerets [2]. Not all of the garden spider’s silks are used in her web. One silk resembles in its function the material of the silk larva, providing the tough covering of the little purse that contains the spider’s eggs. Another silk has a double function: fluffed up it cradles the delicate eggs, but when paid out in ribbons it entangles and enshrouds the unfortunate prey insect. Actually, many silks have multi-purpose: the safety line, trailed at all times, doubles up as material for the frames and radials of the web. The cement that anchors lines to the ground is also used to cement the crisscrossing strands of the egg sac as well as to fix the spirals onto the supporting radials.

Unlike the silk moth’s silk, which provides a tough, protective cover made once in a lifetime, spider web silks are re-spun daily, often in large quantities. They are thin enough to be practically invisible. Yet at the same time they are strong enough to catch insects in full flight, no mean feat considering that, pound for pound, the kinetic energy to be absorbed exceeds the impact of a



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Figure 1. The golden orb spider *Nephila* spp with its silk glands, silks and their mechanical properties.

jet landing in the rubber bands of an aircraft carrier. Some of that energy is absorbed by the material itself while some is deflected by the architecture of the web and some, interestingly, discharged by aerodynamic damping due to the low Reynolds number of the thin threads coupled with a self-assembling micro-windlass system (Figure 2).

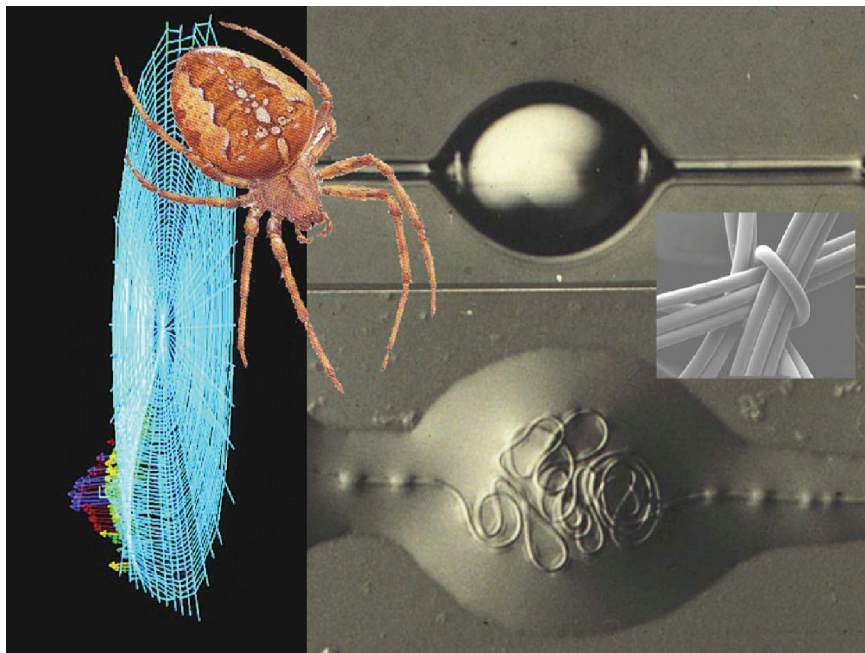


Figure 2. Garden cross-spider with its web and silks, showing the even roundness of the dragline filaments (inset) as well as the wind-lass system inside the droplets of the orb-web's capture thread.

This latter provides interesting (and important) insights into the way Nature works. Essential for the effectiveness of the web are the different mechanical properties of the two major silks used: high strength combined with relative stiffness in the radial spokes of the web and high softness combined with 100% elastic recoil in the circumferential capture spiral. Importantly, the difference in performance properties is in kind not in degree and is due to a simple trick whereby the inherent functional weakness of silk (plastization by water) is turned to advantage. During spinning the spider coats the

naturally dry capture threads with a thin layer of hygroscopic solution, which in turn causes the extraordinary elasticity of the capture spiral in two ways. The hygroscopic solution attracts water from the atmosphere, which, firstly, enters and plasticizes the silk of the thread. Most of the water, however, remains in the coat, which thus forms a liquid cylinder that by swelling rapidly becomes unstable and spontaneously flows into droplets regularly spaced along the core fibres. Each droplet acts as a miniature windlass (powered by its surface tension) by taking up any hysteresis of the core fibres by reeling them in.

Clearly, the performance of an orb web, which is designed by evolution to take out-of-plane load in maximum deflection, is greatly enhanced by incorporating into one web the mechanical properties of different types of silk. Some spiders, like the garden cross spider *Araneus diadematus* have solved the problem of absorbing the high kinetic energy of the insect's impact rather elegantly. This includes the evolutionary invention of a windlass system. Water, is extremely important for spider silks both on the micro-scale level of the mechanical fibre-windlass system and on the nano-scale level of the silk molecules. After all, the windlass "motor" is driven by the surface properties of bulk water while the molecular "motor" is possible because of the mobility of saturated hydrogen-bonds bestowing entropic visco-elasticity.

STRUCTURE-FUNCTION RELATIONSHIPS OF SILKS

Silk, be it spun by spider, moth, mite or bee is basically one and the same material. True, it has evolved independently in the spiders and the insects and differs in the details of its chemistry and production system [3]. However, by the definition of Vollrath & Porter [4], silk is always spun. That sets silks apart from all other biological materials, which are grown. In essence, all silks are composite nano-structured materials consisting of interspersed regions of high, medium and low order, *e.g.* protein crystals embedded in a protein matrix [5]. Different silks differ in molecular composition resulting in different spatial configurations with the nano-scale dimensions giving both strength and extensibility.

This toughness depends not only on the folding of the major silk protein but also on the hierarchical structure of the poly-protein fibre and the conditions under which it is spun. Individual silk fibres range in diameter from 20 to 7000 nm depending on species, spider size, silk type and spinning conditions. The complex hierarchical structure of the fibre is the outcome of a complex spinning process acting on suitable dopants in the polymer feed-stock. The complexity of this process suggests that a number of different

factors contribute to the extraordinary toughness of spider silk. Silk is spun from a highly concentrated (30–50%) solution of large (several hundred kDa) molecules with a highly repetitive molecular structure consisting of alternating sequences of motifs encoding for both rigid and flexible elements. These sequences appear to be folded into a hydrated nano-scale string-of-beads structure that in turn shows liquid crystalline flow behaviour [6].

Silks are natural materials with a range of evolutionary origins and ecological functionalities. But as a rough guide, silk fibres have tensile modulus values in the range 10 kPa for a highly hydrated gel to about 20 GPa for the stiffest dragline silk, and strengths from almost zero values of yield stress to about 1.6 GPa, respectively. Commercial textile silk fibres would have a modulus of about 10 GPa with a strength of about 400 MPa. An important strength parameter is fibre diameter, which might range from about 20 μm down to a few tens of nanometers.

Although silk fibres are very strong, a common misunderstanding about silks is that people think they must also be stiff, which they are not. Generally, spider dragline silks or silkworm silks have modulus values in the range 5 to 15 GPa, which is a factor of 2 to 3 higher than most synthetic amorphous polymers due to the high density of hydrogen bonding, but nowhere near as high as the 100 GPa values for engineering fibres such as PBO. The key to silk properties is the combination of strength and toughness. Interestingly, a model developed to predict the structure-property relations in silk has now been developed to predict the highly nonlinear mechanical properties for any polymer (Porter and Gould 2009), which again demonstrates the power of silk as a model or archetypal polymer to use as a guide to future developments in high performance polymers from sustainable and environmentally benign sources. Perhaps more interesting to paper and cellulose technologies is that such models and concepts might be applicable directly to naturally based cellulose materials with strong hydrogen bonding and the key role of water in both properties and processing, and guides as to how nanostructure can contribute to mechanical properties.

SILKWORM SILKS AND COCOONS

Bombyx mori is a lepidopteran moth species domesticated over millennia for textile silk fibre production. Its cocoons (like those of other silk moths) are natural polymer composite shells with a 3D non-woven structure, consisting of a continuous silk fibroin protein doublet fibre co-extruded with a sericin protein that agglutinates into the composite's matrix material. Such cocoons are made up of several layers that are interconnected but maintain their own

mechanical properties. Figure 3 shows hierarchical scales of morphology in a cocoon, from the cocoon itself, down to the individual sericin-coated fibres, through the nonwoven fibre composite morphology.

Silk fibroin has a semicrystalline structure and accounts for about 75 wt.% in the fibre while silk sericin is an amorphous polymer, accounts for 25 wt.% and acts as an adhesive filler matrix. A typical silk fibre has a strength of about 400 MPa and a Young's modulus of 9 GPa with 35–40% elongation. Sericin, on the other hand, is rather brittle and only tolerates very low strains (about 130 MPa and 6% elongation at a modulus of 4 GPa). Indeed, it seems that sericin properties border brittle and ductile with the failure mode depending on local deformation conditions and the tendency to cavitation for brittle failure and yield for ductile failure.

We believe that silkworm cocoons can be used as a natural model for general nonwoven fibre composites (including paper), so we outline our model here for reference. The observations on the deformation and failure

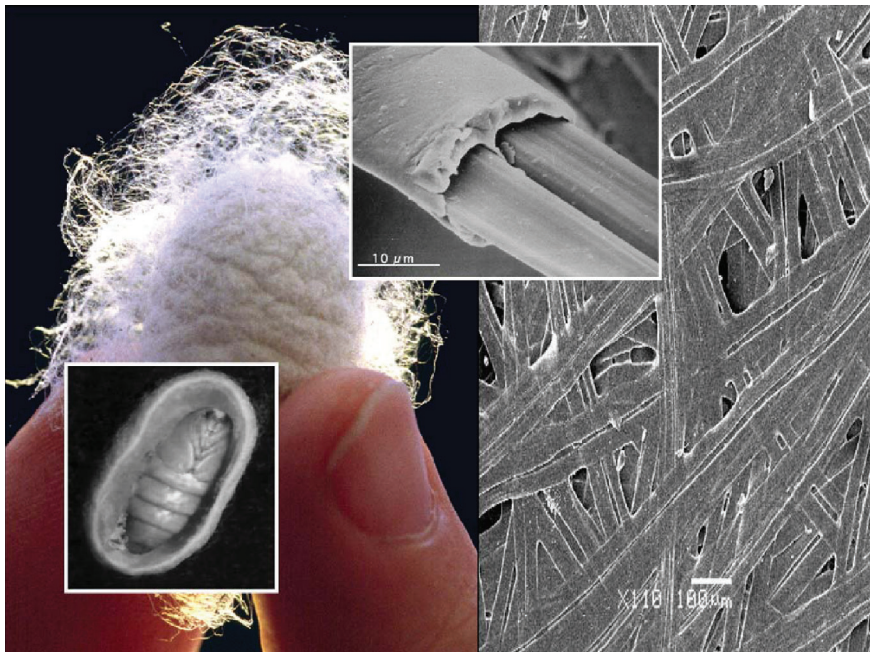


Figure 3. Commercial *Bombyx mori* mulberry-silk cocoon, the pupa of the worm that made it as well as the double-brin bave-structure of a thread and the agglutinated multi-thread wall of the cocoon.

mechanisms in silkworm cocoons suggest very strongly that gradual breaking of bonds between the fibres leads to a reduction in the stiffness of the cocoons. At a critical point, there are not enough bonds to sustain a load in the composite material and the fibres disentangle and pull apart.

We calculate the undamaged modulus of the cocoon, Y , by using an open cell foam model to scale modulus in terms of density relative to that of the solid fibre, Y_f [7,8 and for further references see Figure 4]. The elastic modulus of the cocoon walls was found to follow the open cell foam model of Zhu. This is an extension of the simpler Gibson-Ashby proportionality in density squared and shows how the elastic modulus of the composite is controlled by

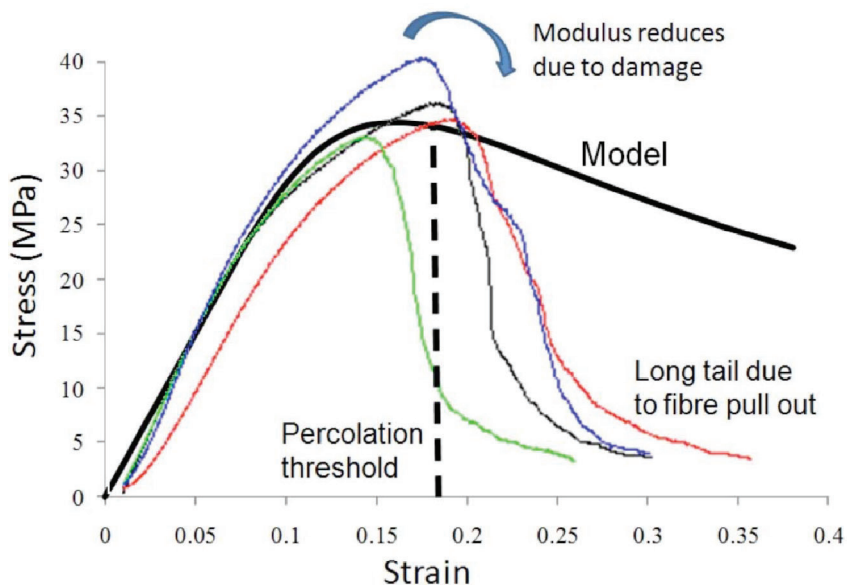


Figure 4. Comparison between observed and predicted stress-strain profile using a modulus of 333 MPa and an activation strain of 0.18, the percolation threshold is reached with a damage fraction of 0.5 a strain of 0.22.

Specific references to Figure 4:

Zhu, H.X., *Analysis of the high strain compression of open-cell foams*. Journal of the Mechanics and Physics of Solids, 1997. 45(11–12): p. 1875;

Gibson, L.J. and M.F. Ashby, *The Mechanics of Three-Dimensional Cellular Materials*. Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, 1982. 382(1782): p. 43–59;

Zallen, R., *The Physics of Amorphous Solids*. 1998, New York: Wiley-VCH.

porosity, where ρ is composite density relative to that of the solid, $\rho_s \approx 1300 \text{ kgm}^{-3}$ and $C_z \approx 1.06$.

$$\frac{Y}{Y_f} \approx \frac{2}{3} C_z \left(\frac{\rho}{\rho_s} \right)^2 \left(1 + C_z \frac{\rho}{\rho_s} \right)^{-1} \quad (1)$$

Key to the open cell foam model is the assertion that the elastic modulus of such a structure is controlled by the bending rather than by the stretching of the fibrous strands between bonding points. This results in the elastic modulus of the material being much lower than its solid tensile modulus.

Then, most importantly, we calculate the breaking strain of a typical sericin bonding site as two fibres cross. We can then scale the bond strength to that of cocoon deformation events by means of the cocoon modulus relative to that of the solid material. From the sericin properties we can assign a linear elastic failure strain for reference purposes of $\epsilon_f \approx 0.033$, then scale this elastic energy density from the sericin to the cocoon to estimate a characteristic activation strain, ϵ_a , in the cocoon that can be associated with bond breaking. Since most of the elastically active material in the cocoon is fibroin with a modulus $Y_f = 9000 \text{ MPa}$ and the cocoon has a modulus of $Y_c \approx 300 \text{ MPa}$, we can scale elastic strain in energy density to suggest characteristic activation strain, ϵ_a

$$\epsilon_a \approx \epsilon_f \sqrt{\frac{Y_f}{Y_c}} = 0.033 \sqrt{\frac{9000}{300}} = 0.18 \quad (2)$$

The bond site strength can then be used as the reference parameter in an activation model to describe the statistical distribution of bond failure events through deformation to a critical percolation threshold point, where there is insufficient connectivity of bonding to sustain load. To a first approximation, the “modulus”, Y , reduces as damage increases in the material with increasing tensile stress or strain as more voids are generated or bonding points are destroyed. Let the damaged fraction be f_d , such that the modulus of the cocoon is taken to be proportional to the undamaged fraction. If Y_o is the undamaged modulus, the reduction in Y with tensile strain, ϵ , relative to the strain associated with an activation energy for damage, ϵ_a , is suggested to have a form of an Arrhenius activation function, where the activation energy and applied energy are taken to be proportional to strain squared,

$$Y = Y_o (1 - f_d) = Y_o \left(1 - \exp \left(- \left(\frac{\epsilon_a}{\epsilon} \right)^2 \right) \right) \quad (3)$$

If we simply take apparent stress, σ , to be (modulus $\times$ strain) at any point, with the parameters Y_o and ε_a obtained either from experimental results or model calculations, we get a relation for the stress-strain profile

$$\sigma = Y \varepsilon = Y_o \left(1 - \exp \left(- \left(\frac{\varepsilon_a}{\varepsilon} \right)^2 \right) \right) \varepsilon \quad (4)$$

The stress falls rapidly at a critical strain soon above the point of maximum stress. Percolation theory suggests that such an effect should happen when there is no connectivity path of bonds through the material to sustain the load. The observed percolation strain is at about 0.22 relative to the activation strain of 0.18. Equation (3) says that this point corresponds to a damage fraction of 0.5, which is of the correct size expected from percolation theory for a bonded lattice. Finally, from observation, the higher strain tail of the stress profile is simply due to the fibres disentangling and the final local bonding being broken. These effects are shown in Figure 4, where the model is compared with observation for a *Bombyx mori* cocoon in the form of a stress-strain profile for the cocoon wall.

Clearly, insect cocoons tend to be solid composite shelters, unlike spider webs, which tend to be light-weight structures. Thus the *Bombyx mori* cocoon is a 3D non-woven structural fibre composite of considerable toughness and one where the mechanical properties of silk fibres and silk sericins interact to form cocoon-wall layers with surprising interfacial fracture mechanics.

OUTLOOK

Silks are amazing materials that consist mostly of protein, are produced by the animal at ambient temperatures and pressures and with water as the only solvent, and yet match or often excel most man-made fibres in material properties. Silks, thus, have many lessons for us in material design. But silks are not only interesting examples for the processes of achieving outstanding material properties. They are also superb examples for the integration of fibres into composites and structures. Accordingly the study of natural silk arrangements is beginning to reveal fascinating insights into ways of making tough composite materials with applications ranging from biocompatible medical implants to high-performance filaments.

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for more references on spiders and silks see www.oxfordsilkgroup.com

Transcription of Discussion

DISCUSSION CONTRIBUTIONS

Chair: Stephen I'Anson

FRC Member and University of Manchester

Gil Garnier Australian Pulp & Paper Institute

Thanks you for a very interesting presentation. What is the upper size limit of a spider's web? I will explain: I am not aware of any spiders catching birds in a web, even in Australia. Why is that? Is the liquid-solid interface critical and do we need evaporation? What is the upper limit, and why do spiders' webs remain very small?

Fritz Vollrath

Spiders do catch birds; there are pictures on a number of websites. However, there is always a suspicion that they are fakes; perhaps the photographer just threw a dead bird into the web! The spider is focused on a very specific prey, and the glue that it uses is very interesting glue and which sticks incredibly well to chitins and things like this. Your question is really why does it not catch birds?

Gil Garnier

With evolution, why did spiders not evolve to grow bigger and catch other bigger animals? Is there a theoretical size limit?

Fritz Vollrath

Size is a different matter. The limitation is not the silk, it is not the web: the critical limit would be the size of the spider because it has an exoskeleton and so has to lug a lot of weight around. The biggest insect that ever grew was the underwater scorpion, which was about 2 metres long, but it was underwater so was supported, otherwise it would be very heavy. An insect with an exoskeleton is rather like a knight wearing armour: the larger he is, the more

surface area has to be covered and the more powerful the muscles needed to move the armour. So the practical upper limit for terrestrial insects would be, I think, the Goliath beetle which is about the size of a fist. Otherwise, of course, they could catch birds, yes; but as it is, the birds catch them.