# SILKWORM COCOON，A BIOLOGICAL COMPOSITE SYSTEM

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## SUMMARY

The cocoon of the commercial silkworm Bombyx mori is used as a model natural nonwoven composite to formulate a model for structural properties of nonwoven composites. The model is based upon open cell foam structures for the intrinsic undamaged elastic properties using the component materials in the cocoon, combined with the effect of gradual loss of connectivity in the interfiber bonding as the cocoon is damaged by increased stress or strain loading. At a critical strain, the bonding connectivity falls below a percolation threshold, and strength falls rapidly to a point where the cocoon is held together by loosely interwoven silk fibres.

*Keywords: silkworm cocoon, biological composite, nonwoven model*

## INTRODUCTION

As part of our work on natural silk materials, we are investigating structure-property-function relations in silkworm cocoons in order to understand the design rules behind this natural nonwoven composite material. These structures have evolved over millions of years by a process of natural selection to sustain and protect moths and butterflies in a wide range of different environments and exposed to many different threats and predators. Since cocoons are very similar in structure to a wide range of nonwoven composite materials, we suggest that understanding of structure and properties in natural cocoons will be a useful guide to understanding those materials and to develop design tools for their optimisation.

The work outlined here suggests a physically realistic model to analyse the properties of cocoons, based upon a very small number of material parameters that can be measured or calculated independently, but which embody all the effects that are observed during the deformation of a cocoon through to failure. Since the same effects are characteristics common to many different types of nonwoven material (ranging from paper to nanofibre mats), we believe that the model will have general interest for the composites community, with perhaps a wider applicability than just for nonwoven composites

### Cocoons: Structure and Properties

Cocoon shells produced by silkworm caterpillars are a kind of natural polymeric composite material in a non-woven structure. It has a similar micro-structure to other stochastic fibrous materials such as paper, nonwoven textiles and electrospun polymer mats.

A cocoon is a natural polymer composite shell made of a single continuous silk strand with a length in the range of 1000-1500m and conglutinated by sericin. Each fibre is composed of two fibroins conglutinated by a layer of sericin. Silk fibroin is a natural fibrous protein with a semicrystalline structure. It accounts for about 75 wt.% in the fibre. Sericin is an amorphous protein polymer that accounts for 25 wt.% and acts as an adhesive to maintain the structure of two fibroins in a fibre and the whole cocoon [1, 2]. Figure 1 shows a hierarchical set of pictures of the cocoon structure, from the full cocoon to the individual fibre-sericin combination.

Research has been carried out on mechanical behaviour of silk fibres, and Zhao et al. have studied the mechanical properties of silkworm cocoons. They measured the tensile properties of the cocoon and the layers, particularly the innermost layer [1, 2, 3].

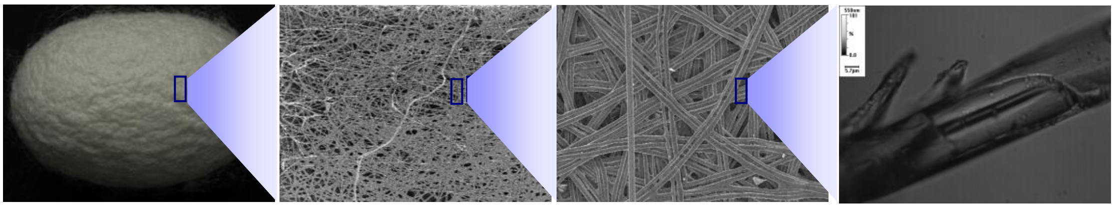

Figure 1 Hierarchy of the morphology of a Bombyx mori cocoon.

A number of typical stress-strain plots for dogbone samples of cocoon walls are shown in Figure 2 for reference, alongside some pictures of the samples during failure. The main observations are that the modulus reduces as the sample is damaged with increasing strain. The main damage appears to be gradual breaking of bonds between fibres up to a strain of about 20%, at which point the stress reaches a maximum value and starts to fall with increasing strain. Soon above the maximum stress, the stress fall rapidly with only small increases in strain. Finally, we observe a more gradual loss of stress, where the fibres gradually disentangle and pull apart in a multi-delamination process, where individual layers in the overall thickness are separated.

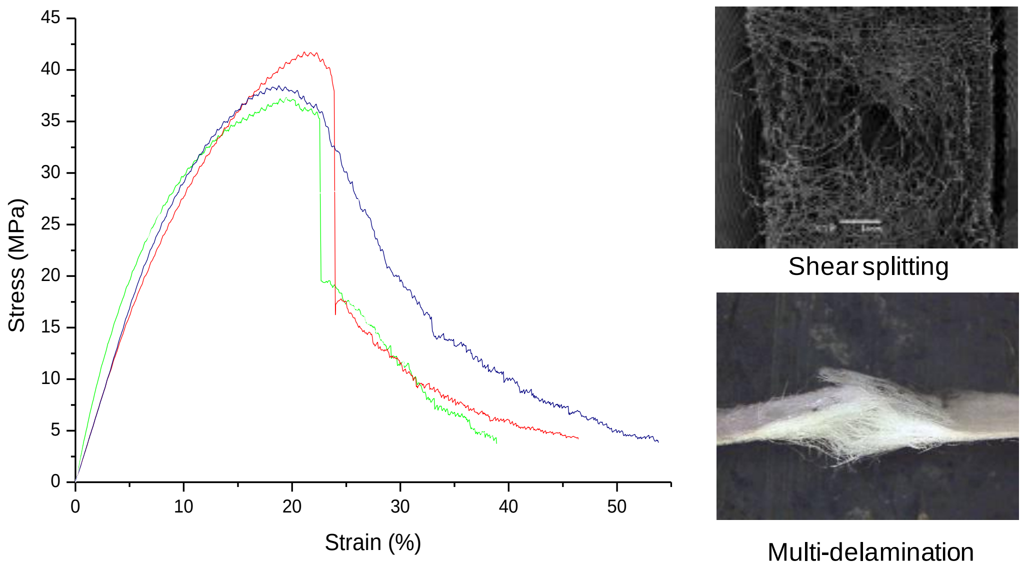


Figure 2 Typical stress-strain measurements on cocoon wall samples, with pictures of cocoons as they fail to illustrate the damage mechanisms.

**Literature Review: strength models for nonwovens**

Although no specific mathematical models could be found for cocoons in the literature, there are a number of strength models for paper, which is also a random fibre network, albeit with a different bonded fibre structure.

Models for the tensile strength of paper, such as the widely applied semi-empirical theory of Page [4] and the mechanistic theory of Kallmes [5, 6], separate the bonding contributions to tensile strength into the influence of the area of inter-fibre bonds that is bonded to other fibres, and that of the shear bond strength per unit area acting in these regions. Calsson [7] suggested that, for short fibre length and low RBA, the mechanism of failure was entirely by bond failure until a threshold of half the theoretical maximum strength of the network; above this threshold, both fibre and bond failure were considered to be involved in rupture. This model does not match all experimental observations.

In a network under strain, the bonded regions of the fibre surfaces facilitate the transfer of stress between fibre segments. This is classic shear-lag theory [8]. Favourable comparisons between Cox's theory and experiments have been reported [9-15], but shortcomings of the shear-lag model have been voiced by Raisanen [16, 17] that the transfer of axial stress in random fibre networks could not be accounted for by the shear-lag approach. Eichhorn [18] observed significant strains at the ends of fibres within the network, contrary to the prediction of Cox that strain would be zero at the fibre ends. S.J.I'Anson [15] suggests that when a network, in which the number of fibres per unit area is just above the percolation threshold, fails under a tensile stress, the dominant mechanism of failure will be that of bonds rather than fibres because the number of contacts per fibre is typically insufficient to transfer enough stress to a fibre for it to fail.

People have sought to relate the strength of paper to its failure by scaling test results from small samples using classic Weibull's theory [19-21]. It states that the strength of samples with no notch is influenced by sample geometry [22] and predicts an exponential decrease in the specific strength of a sample with increasing volume. This dependence arises because the probability of a 'weak-link' in the material under investigation increases with increasing volume. The key point about using a Weibull approach for paper is that failure probability is quantified as a statistical distribution of failure events (bonds breaking) around a stress value that is characteristic for a given material.

## PROPOSAL: STATISTICAL DAMAGE MODEL

The observations on the deformation and failure 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 now need to develop a quantitative model that is physically realistic and embodies this process of bond breaking to predict the full stress-strain profile to failure in terms of the properties of the component materials and the morphological structure of the natural nonwoven composite material.

We will start by describing typical properties for the cocoon component materials of fibres and sericin matrix adhesive and calculate the undamaged modulus of the cocoon by using an open cell foam model to scale modulus in terms of density. Then, most importantly, we calculate the strength of a typical bonding site as two fibres cross. This bond strength will depend upon the size of the bond and we can scale the bond strength to that of cocoon deformation events by means of the cocoon modulus relative to that of the solid material. 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.

**Component Material Properties**

Silk fibres are natural fibroin protein, coated by a layer of about 25% sericin, which bonds the fibres together at crossing points. The elastic modulus of unwashed natural fibres is about 9 GPa, and a typical stress-strain profile to break at about 350 – 400 MPa is shown in Figure 3.

Sericin is thought to be an amorphous protein with a large fraction of serin segments that have an -OH side chain that promotes adhesion. Unfortunately, sericin is very brittle, so experimental measurement of its mechanical properties is quite difficult. Figure 3 also shows a theoretical prediction for the stress-strain profile of sericin [23], which we have seen is very similar to experimental data for amorphous regenerated silk fibres. The key predicted parameters are a low strain modulus of 4 GPa and a tensile yield stress of about 130 MPa. Polymer structure-property relations [24] can be used to estimate the brittle failure stress of sericin to be about 130 MPa, which is the same as the yield stress. Thus, sericin is a typical matrix binder that is right on the boundary between brittle and ductile.

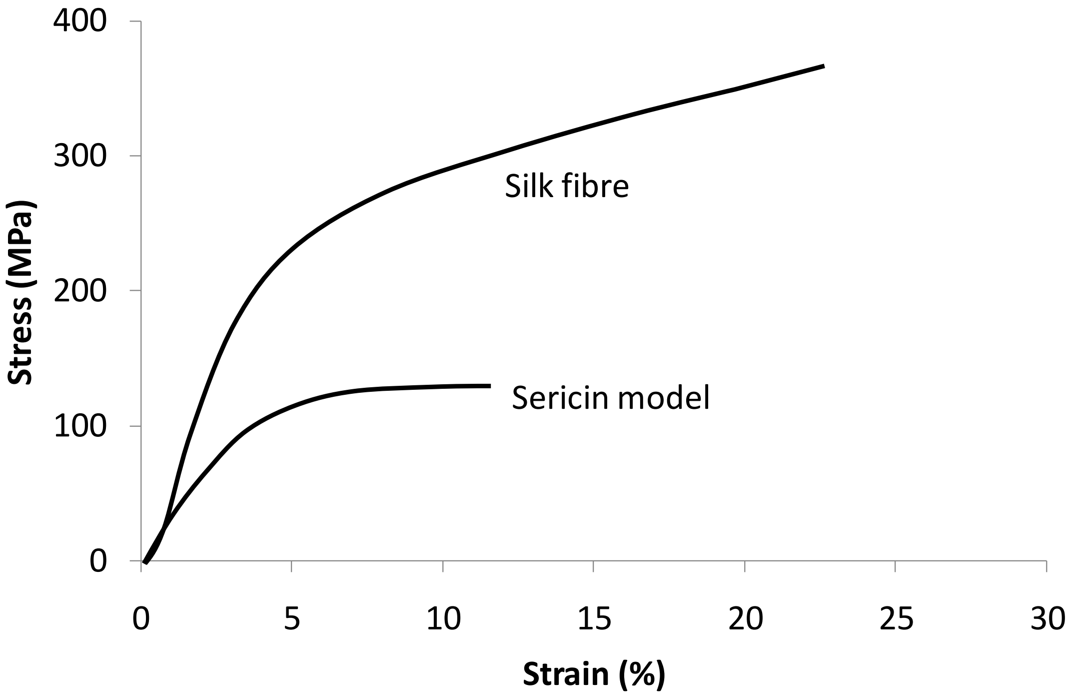


Figure 3 Typical observed stress-strain profile for a Bombyx mori fibre and predicted profile for sericin..

If we take the sericin strength to be 130 MPa with a modulus of 4000 MPa, we can assign a linear elastic failure strain for reference purposes of $\varepsilon_f \approx 0.033$. This is useful, because we can then scale this elastic energy density from the sericin to the cocoon to estimate a characteristic activation strain, $\varepsilon_a$, 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 $Y_f = 9000$ MPa and the cocoon has a modulus of $Y_c \approx 300$ MPa, we can scale elastic strain in energy density to suggest characteristic activation stain, $\varepsilon_a$

$$\varepsilon_a \approx \varepsilon_f \sqrt{\frac{Y_f}{Y_c}} = 0.033\sqrt{\frac{9000}{300}} = 0.18 \qquad (1)$$

This activation strain will become a reference point, relative to which the statistical process of bond breaking in the cocoon can be calculated. This strain suggests that the maximum stress in a cocoon if likely to be of the order of about 50 MPa, since the modulus is about 300 MPa, as shown below.

**Cocoon Modulus: Open-cell Foam Model**

To start the stress-strain profile, we first need to calculate the intrinsic modulus of a cocoon before any damage has occurred. Models are available for morphologically similar materials. Open cell foams allow the free passage of gases between the cells, since the cells consist of strands of material with no film between them to enclose the cells. This is important for cocoons, since it allows metabolic processes such as breathing and water exchange. Models have been developed to provide structure-property relations for such cellular solids. Since most foams do not contain straight-through struts, beam bending rather than stretching comes into play, which leads to relatively low modulus of the material. A simplified 2D model structure for an open cell foam is shown below in Figure 4.

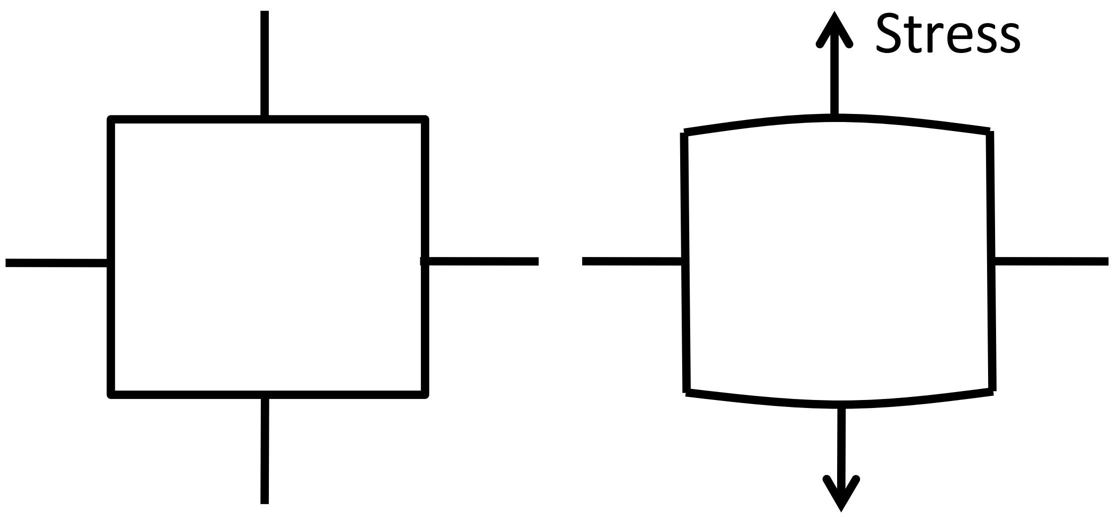


Figure 4 A simplified open cell foam model structure, showing bending of the struts under stress for a low modulus.

Most theoretical attention has been focused on simple three-dimensional cell structures with straight struts (or walls) arranged in periodic arrays at low densities. If the struts are finite, bending is activated at their intersection points and the Young's modulus can be shown to be approximately proportional to density squared [25-27] (n = 2), in general agreement with experimental observation. Zhu [28] and Warren [27] derived analytical results for an open-cell tetrakaidecahedral model packed in a body centred cubic array, which is a very general geometrical form that should be a good representation of a random fibre composite. We applied the relation of Zhu [28] to our cocoons

$$\frac{Y}{Y_f} \approx \frac{2}{3} C_z \left(\frac{\rho}{\rho_f}\right)^2 \left(1 + C_z \frac{\rho}{\rho_f}\right)^{-1} \quad \text{where } C_z = 1.06 \approx 1 \qquad (2)$$

and if $\rho/\rho_s \approx 345/1300 = 0.265$, then $Y/Y_s \approx 0.037$ . For a fibre modulus 9 GPa, then the foam modulus becomes 333 MPa, which is observed.

**Statistical Damage Model**

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, $\varepsilon$, relative to the strain associated with an activation energy for damage, $\varepsilon_a$, 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.

$$Y = Y_o \left(1 - f_d\right) = Y_o \left(1 - \exp\left(-\left(\frac{\varepsilon_a}{\varepsilon}\right)^2\right)\right) \qquad (3)$$

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

$$\sigma = Y\,\varepsilon = Y_0 \left(1 - \exp\left(-\left(\frac{\varepsilon_a}{\varepsilon}\right)^2\right)\right)\varepsilon \qquad (4)$$

Figure 5 shows the model predictions for the stress-strain profile of a cocoon compared to a typical experimental measurement, taken from Figure 2 and using modulus with value of 333 MPa and activation strain with a value of 0.18. We see that the predictions are in good general agreement with observation, except that 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 [29]. 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.

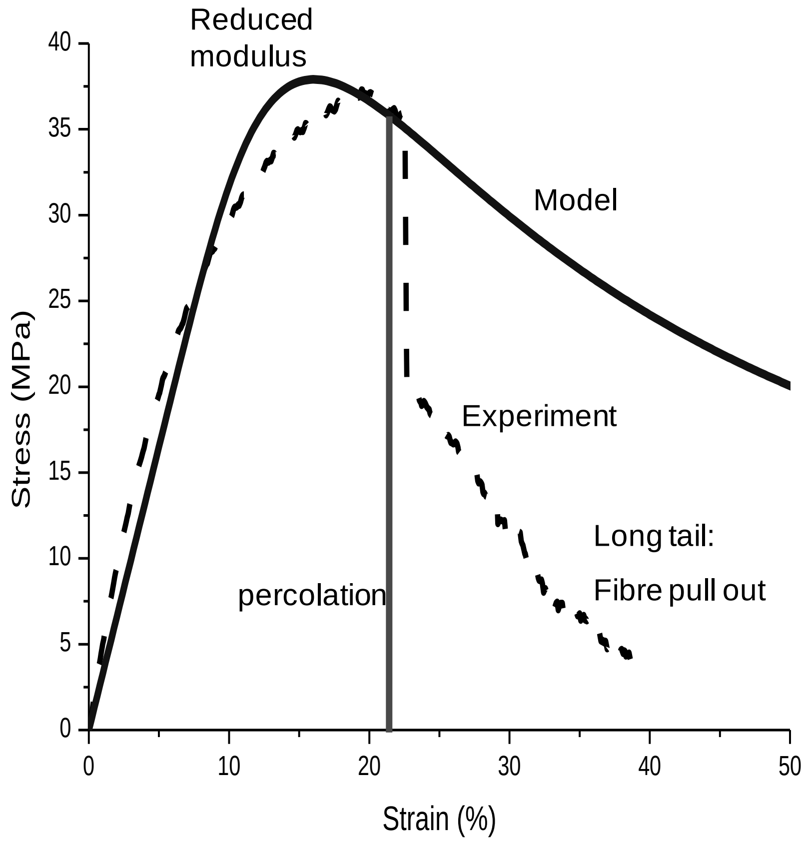


Figure 5 Comparison observed and predicted stress-strain profile using a modulus of 333 MPa and an activation strain of 0.18, the percolation threshold is reached with a damage fraction of 0.5 a strain of 0.22.

## SUMMARY AND DISCUSSION

The model developed in this work is a simple attempt to express qualitative observations on the deformation through failure of a natural cocoon as a physically realistic mathematical model. The main features of a statistical distribution of bond breaking events at the start of deformation, followed my a more rapid fall in stress due to a catastrophic loss in bond connectivity at a percolation threshold are well represented by the model. The model parameters are very simple measures of the undamaged modulus of the composite and a characteristic activation strain that quantifies the central mechanism of bonds breaking. The general agreement between model predictions and experimental observations on the stress-strain profile is good.

The model also embodies all the features required for nonwoven composites that were outlined in the brief literature survey, and has the considerable advantage of being mathematically much simpler than other models. A large number of different cocoon types are found in nature with large differences in their nonwoven-type morphology and property requirements to sustain and protect different kinds of moths or butterflies under a range of different environmental conditions and threats. We hope that future studies of these cocoons will allow us to understand the design rules that nature has evolved over millions of years for optimum performance, and that these design rules will also be useful for synthetic nonwoven composite material design.

The model has also been applied to a very different family of composite materials, namely particulate composites such as concrete and polymer bonded explosives (PBXs) with some success [30]. The same rule of bond connectivity is applied this time to the bonds between particles and binder matrix, and the gradual increase in the number of failed bonds reduces the modulus in the same way.


## ACKNOWLEDGEMENTS

We would like to thank the AFOSR (grant F49620-03-1-0111) for generous funding of our silk research.


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