THE TENSILE BEHAVIOUR OF SPIDER SILK

E. Van Nimmen, K. Gellynck, L. Van Langenhove

Department of Textiles, Ghent University, Technologiepark 907, B-9052 Zwijnaarde, Belgium
Els.VanNimmen@UGent.be
Kris.Gellynck@UGent.be
Lieva.VanLangenhove@UGent.be

Abstract

Spider silk has attracted the interest of several researchers in recent years because it displays a unique combination of high tensile strength, high breaking strain and an ultra-low weight. Hitherto, the focus has always been on dragline and viscid silk, whereas research on spider cocoon silk is limited. In order to explain the structure-property relationship of spider silk, the stress-strain behaviour of cocoon and dragline silk is compared in this study. It is shown that both fibres have completely different stress-strain behaviours.In addition, the influence of the testing speed is investigated. For cocoon silk, lower testing speeds result in lower strength, stiffness and higher post-modulus. When the stress-strain curve is simulated by an extended Maxwell model, as testing speed increases, the level of the hardening region is higher, the yield region moves to higher strains and the hardening region in the stress-strain curve becomes more horizontal. However, a speed of 20 mm/min can be considered as a saturation point where the effect of the speed decreases. The influence of the testing speed on dragline silk is clearly less pronounced than for cocoon silk. However, a more detailed study of the stress-strain curves of dragline revealed different possible shapes for the stress-strain behaviour of dragline silk.

Key Words:

Spider silk, dragline, cocoon, stress-strain

1. Introduction

In recent years, spider silk has gained more attention because spider silk, and particularly the 'dragline' thread, is a fibre with a unique combination of high tensile strength, high strain and an ultra-low weight. Table 1 gives an overview of the different spider silks for *Araneus diadematus*, their glands, their function and amino-acid composition.

Table 1. Types and functions of spider silk for *Araneus diadematus* (reproduced from [1])

Silk	Gland	Function	Amino-Acids[a]
Dragline	Major ampullate	Orb web frame, radii, ampullate	Gly (37%), Ala (18%), small side safety line chains (62%), polar (26%)
Viscid	Flagelliform	Prey capture, sticky spiral	Gly (44%), Pro (21%), small side chains (56%), polar (17%)
Glue-like	Aggregate	Prey capture, attachment	Gly (14%), Pro (11%), polar glue (49%), small side chains (27%)
Minor	Minor ampullate	Orb web frame	Gly (43%), Ala (37%), small side chains (85%), polar (26%)
Cocoon	Cylindrical (tubuliform)	Reproduction	Ser (28%), Ala (24%), small side chains (61%), polar (50%)
Wrapping	Aciniform	Wrapping captured prey	Ser (15%), Gly (13%), Ala (11%), small side chains (40%), polar (47%)
Attachment	Piriform	Attachment to environmental substrates	Ser (15%), small side chains (32%), polar (58%)

(a Small side chains = Gly + Ala + Ser, polar = Asp + Thr + Ser + Glu + Tyr + Lys + His + Arg)

Spiders produce a variety of silks that range from rubber-like elastic fibres to Kevlar-like superfibres, but it is not known how spiders modulate the mechanical properties of silks. Most of the spider silks that have been studied are silks provided by the major ampullate (MA) glands, used by the spider to form the web frame and the spider's dragline (strength 1.1 GPa – breaking strain 27% [2]). Another truly remarkable spider silk that is often investigated is the viscid silk (strength 0.5 GPa – breaking strain 270% [2]) that is secreted by the flagelliform glands, and forms the glue-covered catching spiral.

Up to now, the amount of literature on spider cocoon silk has been rather limited. Since it could help to explain the structure-property relationship of spider silk, a comparison in this article is made between the tensile behaviour of dragline silk and cocoon silk of *A. diadematus*. Moreover, the influence of the testing speed is discussed.

2. Difference Between Dragline And Cocoon Silk

2.1 Materials and methods

Five cocoons of *Araneus diadematus* were collected in a garden house. One hundred fibres were gently torn out of each cocoon and tested.

For the dragline samples of *A. diadematus*, some spiders were maintained under controlled conditions in the laboratory, and thirty samples of dragline thread were manually reeled off. From every sample, ten fibres were prepared and tested.

The Favimat-Robot (Textechno) was used to analyse the tensile properties of the cocoon fibres and dragline threads.

It is a semi-automatic single strength tester, working according to the principle of constant rate of extension (DIN 51221, DIN 53816, ISO 5079). It allows the force to be measured at a high resolution of 0.1 mg.

Moreover, this instrument is equipped with an integrated measuring unit for linear density (in dtex). This has the considerable advantage (certainly for natural fibres) that the fineness is determined simultaneously with the tensile properties.

The linear density is measured according to the vibroscopic method (ASTM D 1577 – BISFA 1985/1989 chapter F).

Because of the extreme fineness of the dragline thread, it was unfortunately not possible simultaneously to determine the fineness for the draglines. The fineness (in µm) was measured on a high number of samples with image analysis on a light microscope; the conversion was made to dtex by taking into account a specific density of 1.3 g/cm³, according to the method which can be found in the literature [3].

The tensile properties were tested with a gauge length of 20 mm, a test speed of 20 mm/min, and a pre-tension of 0.5 cN/dtex. For the linear density, a test speed of 5 mm/min and a pretension of 0.8 cN/dtex were applied.

2.2 Results and discussion

As is shown (Figure 1), cocoon silk shows a completely different stress-strain behaviour; although the strain to break is more or less the same (± 30%), the tenacity is 3.5 times higher for dragline silk. It is also remarkable that the stress-strain curve of cocoon silk shows a logarithmic behaviour, which is not the case for dragline silk. Comparing the amino-acid composition of both spider silks, it may be noted that the high glycine-portion, typical for the dragline, may partly explain this behaviour. Further research on the microstructure of spider silks is required in order to further reveal the secrets of spiders.

3. The Effect Of Testing Speed For Cocoon And Dragline Thread

3.1 Materials and methods

Some hundreds of *A. diadematus* spiders were maintained under controlled conditions in the laboratory. Four different cocoons were selected randomly, and the eggs were carefully removed from each sample. For each test, 50 fibres were gently torn out of each cocoon.

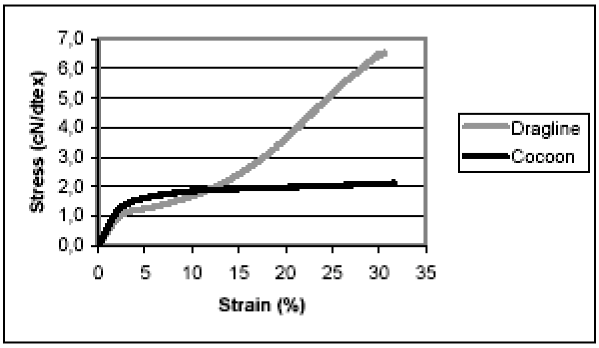

Figure 1. Stress-strain behaviour of cocoon and dragline spider silk of *A. diadematus*

Different samples of dragline thread were manually reeled off. Samples of three different spiders were selected, and 50 fibres were taken for each test.

For this study, since we are interested in the influence of the testing speed, the fineness of the dragline threads was not determined, hence the force values (in cN) were considered.

The fibres and filaments were tested with the Favimat-Robot using a gauge length of 20 mm, a pre-tension of 0.5 cN/dtex and 5 different speeds: 5, 10, 20, 30 and 40 mm/min. For the dragline threads, only the tests for speeds of 5, 20 and 40 m/min were performed, because of a lack of material taken from the same spider at the same moment.

For each of the cocoons and draglines, the stress-strain curves were characterised by the following parameters :

1. **Breaking stress or tenacity**: the ratio of a yarn's breaking force to its linear density, in cN/dtex.
2. **Strain at break**: the increase in the length of a specimen produced by the breaking force, expressed as a percentage of the original nominal length, in %.
3. **Work to rupture**: the area contained by the force/elongation curve up to the point where the breaking force is reached, cN.cm. This is a measure of the toughness of a fibre.
4. **Initial modulus**: defined as the modulus in the elastic range of the diagram in which strain changes are still reversible, in cN/dtex. This is calculated from the slope of the initial straight line portion of the stress-strain curve.
5. **Post modulus**: defined as the modulus between the strain values of 10 and 35%, characteristic for the relatively linear hardening region, in cN/dtex.

For a further discussion of the results, the Maxwell model is used to describe the tensile test. In this model, the fibre is represented by a model with elements that show a certain time-dependent mechanical behaviour, namely by means of a combination of springs and dashpots. The dashpot represents the time-dependent, viscous behaviour.

In the simplest Maxwell model [4], the elasto-viscous behaviour of a fibre (or yarn) is described by a spring (with elastic constant E) and a dashpot (with a damping constant or viscosity η) in series. This behaviour obeys the following equation (with ε the strain and F the force):

$$\frac{d\varepsilon}{dt} = \frac{1}{E}\frac{dF}{dt} + \frac{F}{\eta} \qquad (1)$$

For a constant increase of strain with time, we can assume/state that ε = r t, with r a constant, so that Equation (1) becomes:

$$r = \frac{1}{E}\frac{dF}{dt} + \frac{F}{\eta} \qquad (2)$$

with F(0)=Fv as the starting condition, and Fv the preload, the following solution is found:

$$F(\varepsilon) = F_v + \eta \cdot r \cdot \left(1 - e^{-\frac{E}{\eta \cdot r}\varepsilon}\right) \quad (3)$$

The formula can be written as:

$$F(\varepsilon) = F_v + A \cdot \left(1 - e^{-B\varepsilon}\right) \quad (4)$$

From the experimental results, we can conclude that this Maxwell model does not completely satisfy the simulation of the stress-strain curve of the cocoon silk fibres. It was proved that an extended Maxwell model, by adding a linear spring, allows a better simulation of the stress-strain curves of cocoon silk. Equation (4) can then be written as follows :

$$F(\varepsilon) = F_v + A \cdot \left(1 - e^{-B\varepsilon}\right) + C \cdot \varepsilon \quad (5)$$

By means of a non-linear regression, the stress-strain curves can be characterised by 3 parameters A, B and C. With the data of the stress-strain curves of cocoon silk, determined above in 2, a correlation of higher than 99% with a relative error smaller than 0.1% was most frequently observed. The effect of the test speed is also discussed on the basis of these parameters.

3.2 Results and discussion

3.2.1 Influence of speed on strain at break, tenacity, work to rupture, initial modulus and post-modulus

The first remark that should be made is that all parameters show a high variation. For strain to break and work to rupture, the CV value even exceeds 30%; for the moduli values, this CV-value is in most cases restricted to 10-15%, and for tenacity, the CV is mostly between 10 and 15%. The high variability (intra-species and intra-individual) is confirmed by other authors [5-6].

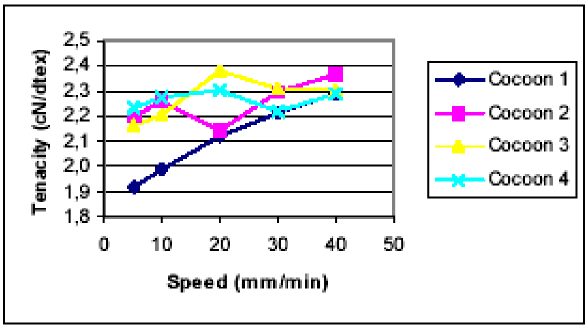

Figure 2. Influence of speed on tenacity

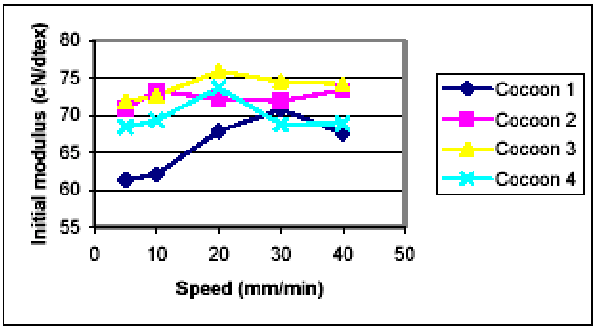

Figure 3. Influence of speed on work to rupture

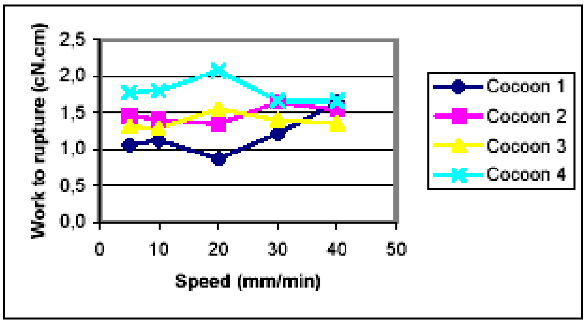

Figure 4. Influence of speed on initial modulus

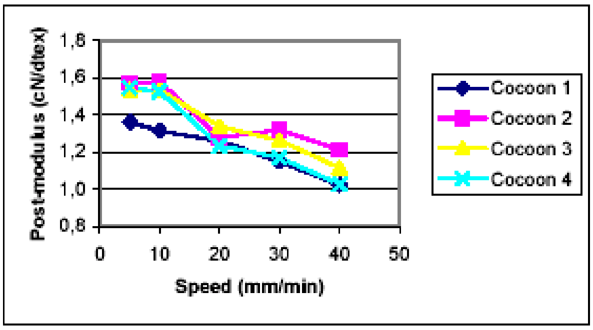

Figure 5. Influence of speed on post-modulus

For strain at break, an analysis of variance reveals that the testing speed has no significant influence. Figures 2 to 5 represent the influence of the speed on tenacity, work to rupture, initial modulus and post-modulus respectively. It can be concluded that for most parameters, no general conclusion that is valid for all cocoons can be drawn.

In respect to tenacity, for the average of all cocoons, it can be concluded that tenacity increases with the increase of testing speed.

Moreover, a significant logarithmic correlation (R^2=0.9797) can be found between both parameters, as is shown in Figure 6.

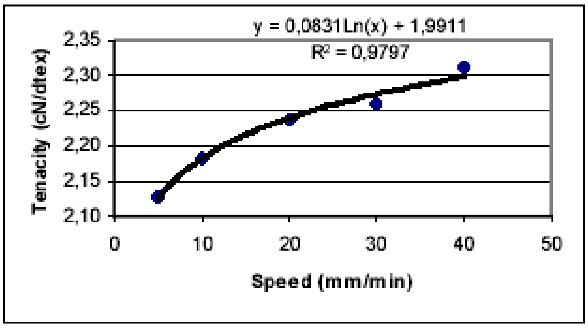

Figure 6. Logarithmic increase of tenacity with speed

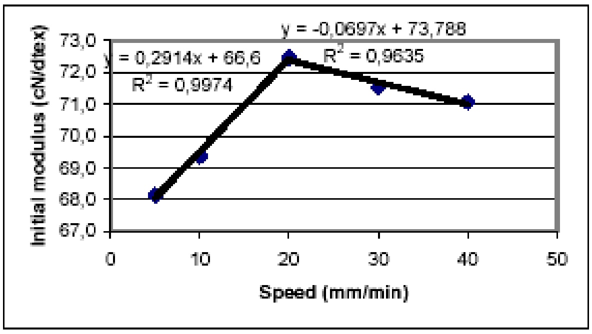

Figure 7. Relationship between initial modulus and speed

When all the cocoons are considered together, the initial modulus increases with the testing speed until a speed of 20 mm/min is attained, followed by a decrease with a higher testing speed, as is represented in Figure 7. This is surprising, since in the literature an increase of elastic modulus with speed has been observed [7]. Since the initial modulus is correlated with the microstructure of a fibre, it seems that during tensile deformation some conformational changes occur that may relax over a longer testing time or at a lower testing speed.

Finally, it is seen in Figure 5 that the post-modulus, and thus the modulus of the hardening region, decreases with the testing speed. This is confirmed by a significant decrease (R^2=0.9637) of the post-modulus with the testing speed when calculating the average post-modulus for each speed.

For draglines, no statistically significant influence of speed could be found for strain to break, breaking force, work to rupture or post-modulus (10-25%). For the initial modulus alone, the value for the speed of 5 mm/min is significantly higher than for the speeds of 20 and 40 mm/min. In summary, it can be concluded that the influence of speed is less pronounced for dragline silk than for cocoon silk.

From a more detailed study of the stress-strain curves, different shapes of curves could be observed (Fig. 8). The Type 1 curve is in most cases the most frequently occurring curve; sometimes two groups with different initial slope are observed. The Type 2 curve is characteristic for cocoon spider silk. The Type 3 curve is an almost linear curve, but is rarely found.

The reasons for these different types of curves are not clear yet. This should be investigated further.

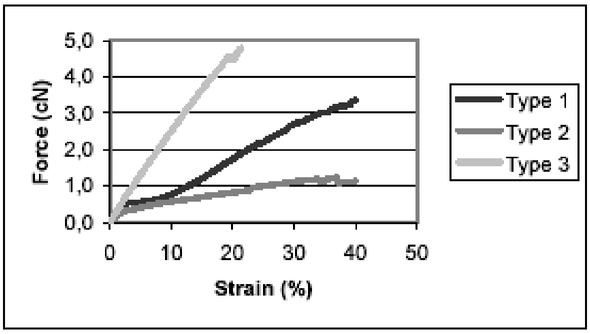

Figure 8. The three types of stress-strain curves occurring for dragline silk

3.2.2 Parameters A, B, C of the extended Maxwell-model

Figures 9-10-11 show the influence of speed on the parameters A, B and C of the extended Maxwell model for the cocoons, as represented by Equation 5.

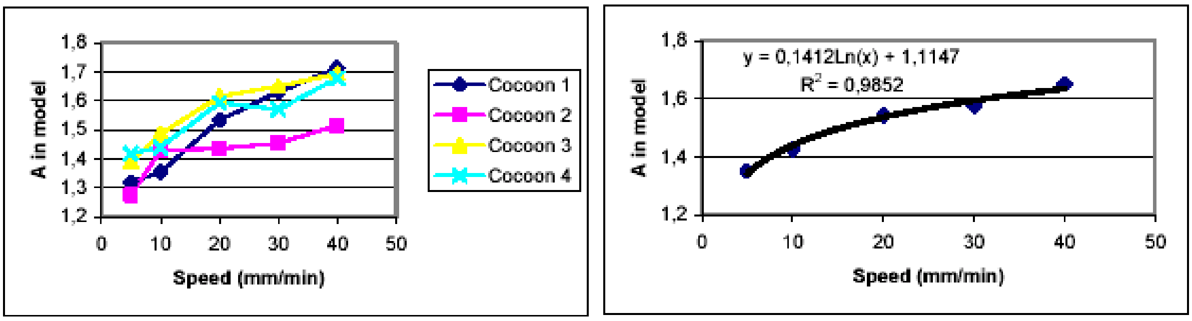

Figure 9. Influence of testing speed on parameter A in extended Maxwell model

As can be seen in Figure 9, the parameter A logarithmically increases with the testing speed. Since changing parameter A results in a curve with a higher maximum level of the hardening region (a fairly horizontal part), this is in accordance with the result for tenacity. Moreover, parameter A also results in a change of initial modulus. In this respect, it should be remarked that for speeds higher than 20 mm/min, the increasing effect of A with speed is minimal; however, it does not seem to decrease, as is observed for the initial modulus.

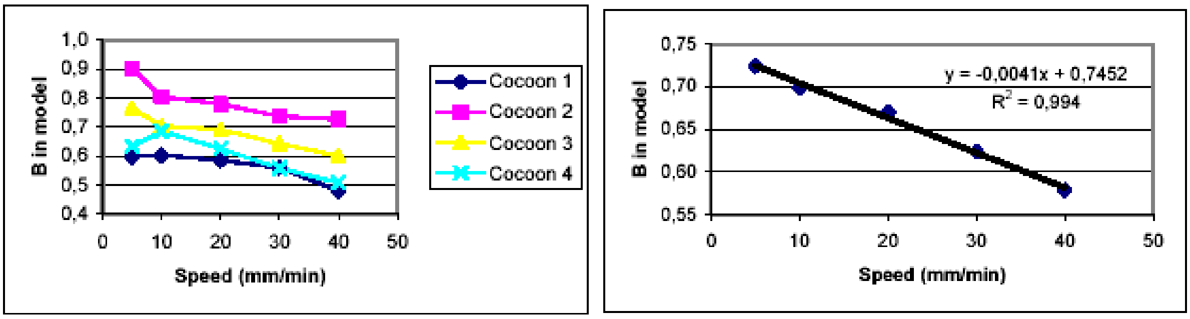

Figure 10. Influence of testing speed on parameter B in extended Maxwell model

Parameter B significantly decreases with the testing speed. The value of parameter B represents the shape of the yield region.

The yield point moves to higher strains, and as a result the initial modulus decreases, as B decreases.

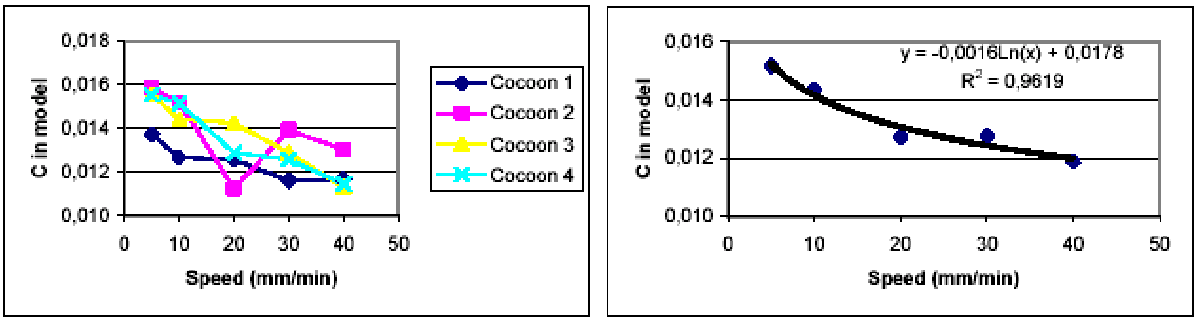

Figure 11. Influence of testing speed on parameter C in extended Maxwell model

Also, parameter C logarithmically decreases with the testing speed. Here as well it should be remarked that for speeds higher than 20 mm/min, the influence of the speed on C decreases. An increase of C in Equation (5) results in a steeper slope, and thus a higher post-modulus. The influence of speed on parameter C is more or less in accordance with the result for the post-modulus.

Conclusion

First of all, it can be concluded that cocoon silk shows a completely different stress-strain behaviour than dragline silk, although the resulting breaking strain is more or less the same.

Looking at the effect of the testing speed, it has been demonstrated that at low testing speeds, the tenacity, work to rupture, toughness and stiffness will be lower, while the post-modulus will be higher than at high testing speeds. A sort of 'breaking point' occurs at a testing speed of 20 mm/min. This can be explained by the fact that at lower speeds a certain amount of plastic or unrecoverable deformation takes place during the time of the test itself, due to changes in the structure, which is not the case at high testing speeds.

When the stress-strain curve of cocoon silk is simulated by means of an extended Maxwell model, higher testing speeds result in a higher level of the hardening region, a movement of the yield region to higher strain values, and a more horizontal behaviour of the hardening region. A speed of 20 mm/min can be considered as the saturation point from which the effect of speed decreases.

The influence of the testing speed for dragline silk was clearly less pronounced than for cocoon silk. However, it should be taken into account that different shapes of stress-strain curves within each dragline were observed, which cannot yet be explained.

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