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Mechanical properties of dragline and capture thread for the spider *Nephila clavata*

M. KITAGAWA, T. KITAYAMA
Mechanical Systems Engineering, Kanazawa University, 2-40-20 Kodatuno, Kanazawa, Japan

Mechanical properties of the dragline and the capture thread for the spider *Nephila clavata*, called Jorougumo in Japan, were investigated and the effect of ultraviolet rays and acid rain on their strength was studied to consider the applicability to the environmental assessment of the habitat of the spider. It was shown that (1) the dragline, which has a fracture stress of about 1500 MPa, a fracture strain of about 0.3 and a modulus of about 10 GPa, is almost equivalent to the best man-made fibres such as aramid fibres, (2) the load–strain curve for the capture thread is J-shaped and its fracture strain amounts to more than 200%, whereas the endurance load is much smaller than that for the dragline, (3) a wonderful mechanism for the capture thread termed the ''windlass system'' by Vollrath and Edmonds, was reconfirmed, and (4) the irradiation by ultraviolet rays and exposure to quasi-acid rain induced degradation of the thread.

1. Introduction

Spiders use different kinds of silk, produced by several spinnerets on their abdomens, for special purposes [1, 2]. The orb web is constructed from radial and spiral lines (capture threads) with distinctive mechanical properties. The threads which constitute the frame and radii of the orb-web are produced by the major ampullate glands. The dragline upon which the spider lowers itself is also produced by the same glands. The viscid spiral, which is used to catch insects, is produced by the minor ampullate glands.

Spider silk is an attractive material for the following reasons. (1) Because the threads are used to catch flying insects, they are expected to be a high-performance fibre, and (2) compared with man-made fibres spun under high temperature or dangerous solvents, they are safe and gentle to both mankind and the earth, being produced by the organs of the living arachnid. Thus, the threads from spiders may be one of the best structural materials produced by nature.

Various reports have been published on the mechanical properties [3–8], X-ray analysis [9, 10], and biochemical studies [11, 12] of spider silk. But less attention has been paid to their mechanical properties in contrast to those of cocoon silk fibres made by the silkworm.

In this work, the mechanical properties of the radial and spiral threads of the orb-web woven by *Nephila clavata*, were investigated and the effect of ultraviolet rays and acid rain on their strength was also studied in order to consider their applicability to the environmental assessment of the habitat of the spider.

2. Experimental procedure

2.1. Preparation of specimens

The spiders *Nephila clavata*, called Jorougumo in Japan, were collected at different dates between July and October, in a small park near to our university and were bred in cubic chambers with dimensions 500 mm × 500 mm × 500 mm where the spiders could weave the orb-webs.

A bundle of the draglines was automatically reeled at a speed of about 50 mm s^{-1} from the spiders with 15 mm × 30 mm wire frames using a home-made machine. These samples were used for the tests on the degradation due to ultraviolet (UV) irradiation. Tensile specimens of the dragline were taken directly from the spiders. The threads upon which the spider lowers itself were attached to paper tabs with a square window 15 mm × 15 mm using a double-faced adhesive tape, as shown in Fig. 1.

The capture spirals were taken using large-framed papers from the orb-webs woven in the breeding chamber. Tensile samples were made by attaching the capture threads to the framed paper by the paper tabs, with a window 7.5 mm × 15 mm.

The samples were inspected using an optical microscope, and only clean samples, which were not torn off and were covered very little by small dust particles, were used for the tests.

2.2. Microscopic examination

The surfaces of both the draglines and the spiral lines were observed by scanning electron microscopy (SEM). In order to examine the cross-section of the draglines, a bundle of them was pasted on thin paper

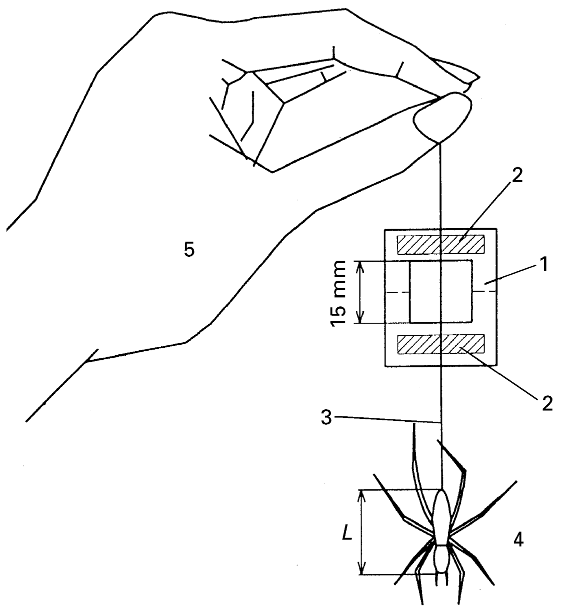


Figure 1 Method for making tensile specimens of spider dragline. 1, Thin framed paper; 2, double-sided adhesive tape; 3, dragline; 4, spider *Nephila clavata*; 5, hand.

with a sharp side-cut, and was broken in liquid nitrogen in a brittle fashion together with the base paper.

The draglines were ion-etched in argon gas at a vacuum of 2×10^{-2} torr (1 torr = 133.322 Pa) at a power of 10 W for 3 min, to estimate the rough structure of the crystalline and amorphous regions.

2.3. Tensile tests

The tensile tests were executed using a home-made machine with a load cell of 10 g for testing the dragline and 2 g for testing the capture thread. After a sample was attached to the testing machine, the centres of the paper frame were cut off using scissors, and the initial force was removed, and the tensile tests began at a speed of $0.25\ \mathrm{mm\,s^{-1}}$ at room temperature, $20 \pm 3\ ^{\circ}\mathrm{C}$. The gauge lengths for the dragline and the capture thread were 15 and 7.5 mm, respectively. The data obtained were arranged by a nominal stress and a nominal strain or draw ratio.

2.4. Irradiation by ultraviolet rays (UV)

The webs woven by spiders in nature may be degraded by environmental pollution, such as UV, acid rain, acid mist, exhaust gas, and so on, by which their inhabitable environment may be more or less affected. In this work, the effect of the UV irradiation and acid rain on the degradation of the dragline was investigated. The specimens mentioned above were exposed to UV at room temperature, 25 °C, for 1–24 h on a UV generator (peak wavelength 302 nm, power 90 $\mathrm{W\,m^{-2}}$), and were pulled at a speed of $0.25\ \mathrm{mm\,s^{-1}}$. The bundles of draglines coiled round a wire frame were also exposed to UV and their dynamic properties were measured at a temperature increase rate of 5 °C $\mathrm{min^{-1}}$ and at 1 Hz, under a constant tensile load using an Orientec Reovibron dynamic mechanical analyser.

2.5. Effect of acid rain

Quasi-acid rain, consisting of sulphuric acid and distilled water, was prepared with various concentrations of acidity, pH 1–4. After the dragline specimens were wetted during arbitrary periods from 1 h to 1 week, they were pulled at a tensile speed of $0.25\ \mathrm{mm\,min^{-1}}$.

At present, the concentration of acid rain is about pH 5 at most, and acid rain with an acidity stronger than pH 4 is not considered to fall. However, in a case where the water escapes in a vapour, an acidity stronger than pH 4 may be realized. For an acid mist, an acidity of about pH 2.5 has been reported at present everywhere in the world [13].

3. Results and discussion

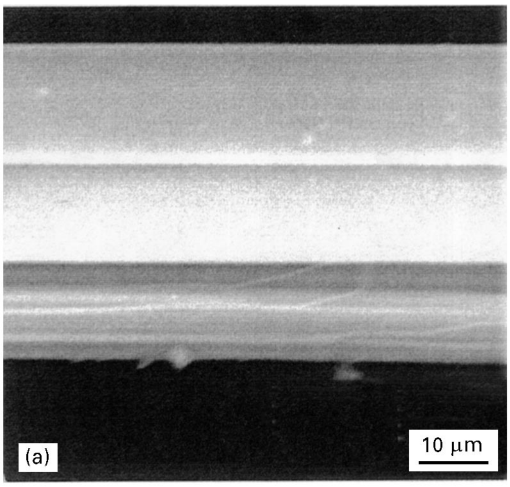
3.1. Fibre morphology

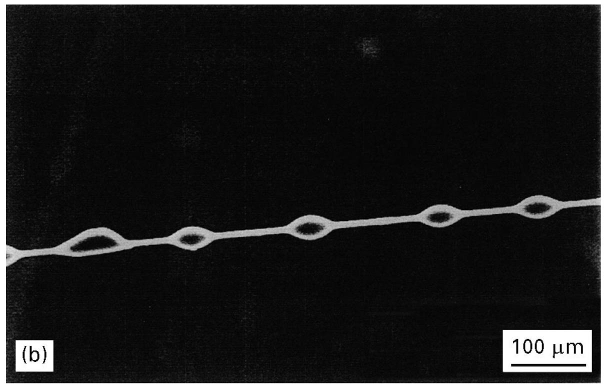
Fig. 2a and b show the surface morphology of the draglines and the spiral lines, respectively. The draglines are smooth without any characteristic markings. The spiral lines have a series of regularly spaced droplets distributed along the fibre axis. These droplets consist of viscid liquid used to catch insects.

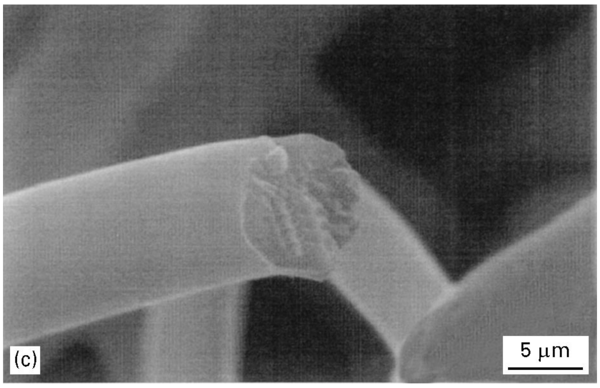
The cross-section shown in Fig. 2c, which is broken in liquid nitrogen, is nearly circular, in contrast to that of the silkworm threads which have nearly triangular shapes. Therefore, it seems possible to calculate the cross-sectional area by measurement of the thread diameter with probable accuracy. The fracture surface is covered by river markings indicative of brittle fracture. The surface is uniform and no difference in the markings between the outer and inner layers of the cross-section is observed on the brittle fracture surface. Therefore, the structure of the fibre is supposed to be uniform over the cross-section, in contrast to the fibre of the silkworm which consists of sericin in the centre and fibroin surrounding it [14].

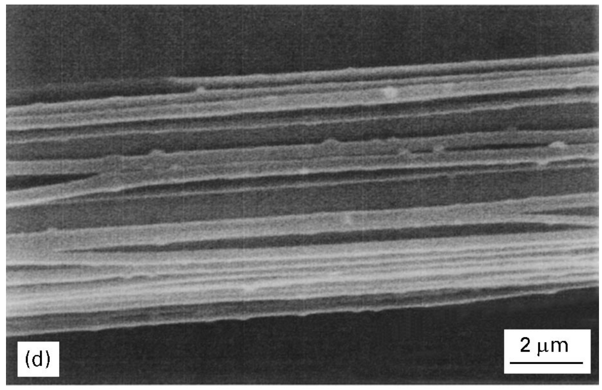
An area part accidentally abraded along the fibre is shown in Fig. 2d. Many micro-fibrils exist with a diameter of about 0.1 μm even at considerable depths from the outer surface. This may indicate the presence of a fibrillar structure, in contrast to the results observed by Mahoney *et al.* [9]. They, using an atomic force microscope (AFM), suggested that because the marks similar to a fibrillar structure were not continuous along the longitudinal direction, and the depths of the channels caused by these marks were too shallow to indicate definitely independent fibrils, the existence of those marks did not always signify the presence of a microfibrillar structure. On the basis of this observation, they concluded that even when the dragline was bent sharply at a small curvature, of the order of the fibre diameter, no kinking and no tensile breaking initiated at the inner compressive surface. Therefore, the dragline fibre was strong compared to the man-made fibres such as aramid and carbon fibres. However, their photographs are not as clear as Fig. 2d, and therefore the absence of a fibrillar structure may not be proved to be true.

The ion-etched pattern of the draglines is shown in Fig. 2e. A series of small granules of size 20–50 nm, are arranged parallel to the fibre axis. These granules, unetched by the ion-etching, are considered to consist









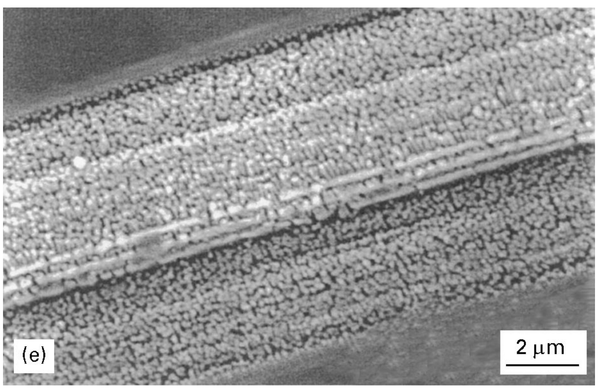


Figure 2 Surface morphology of dragline and capture thread. (a) Draglines, (b) capture threads, (c) cross-section of dragline broken in liquid nitrogen, (d) abraded part of draglines, and (e) ion-etched draglines.

of a structure with a strong cohesive force, that is, a crystalline region. The degree of crystalinity may be roughly estimated.

3.2. Stress–strain response of the dragline

Load–strain curves are shown in Fig. 3 for the *Nephila clavata* spiders, taken at different dates from July to October. The strength is much stronger for the fibres taken in October than those taken in July, because the fibre diameter for the spiders in October is about 2.5 times larger than that in July. The load at fracture was found to be nearly proportional to the square of the body length, and hence the square of the thread diameter (see [6]). Therefore, the ability to catch insects is found to increase sharply with an increase in the body length. Whether or not the knee points seen at a strain of about 0.05 correspond to the yield point, is not known.

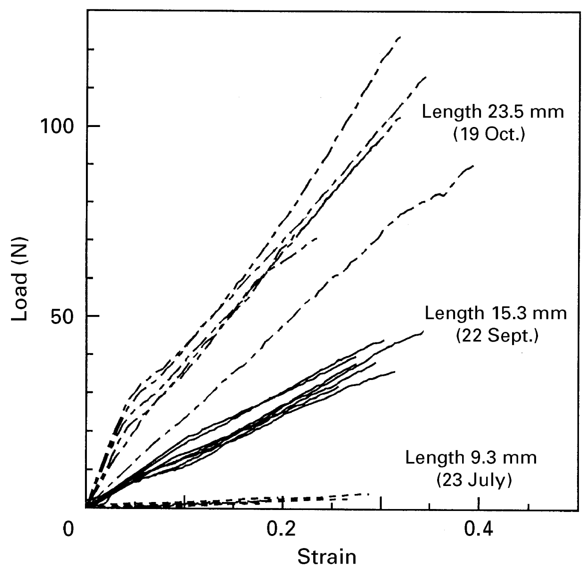


Figure 3 Load–strain curves for draglines of spiders taken at different periods.

These data are rearranged on a stress–strain diagram in Fig. 4. All the curves fall in a small range, in contrast to the load–elongation curves. This may mean that the stress–strain response is independent of the season when the threads were collected from the spiders, and therefore probably the composition and the structure of the fibres are not varied much by the body length of the spider.

The stress and the strain at fracture are plotted as a function of the body length of the spider in Fig. 5, in

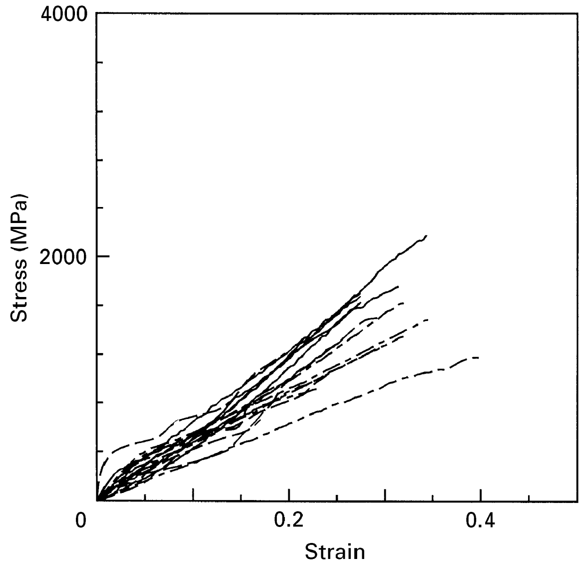


Figure 4 Stress–strain curves for the same data as used in Fig. 3. Lengths: (– – –)9.3 mm, 23 July; (——) 15.3 mm, 22 September; (— —) 23.5 mm, 19 October.

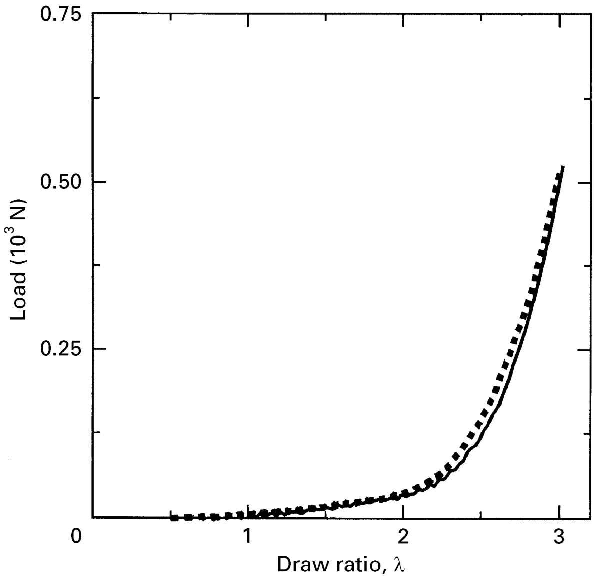


Figure 6 A typical example of load–draw ratio curves for capture thread. (——) The curve for the capture thread taken from the orb-web. (– – –) The curve obtained when the thread is contracted to half the original gauge length and pulled again.

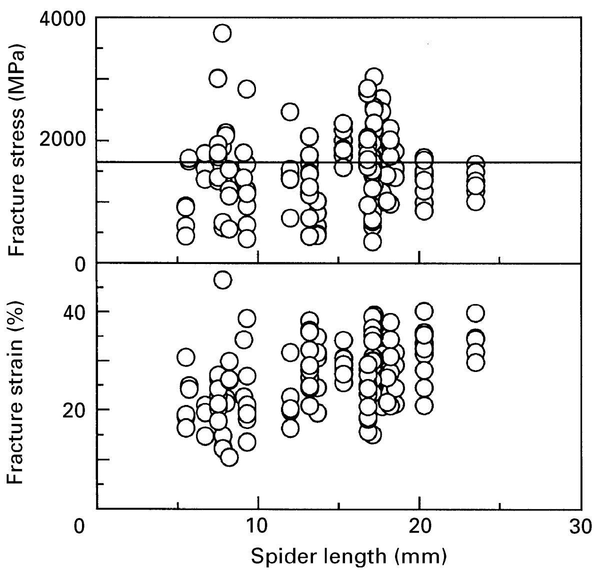


Figure 5 Fracture stress and fracture strain as a function of spider length for dragline.

which all the data tested in this experiment are given. The considerable dispersion of the data may be attributed mainly to the inaccuracy of the fibre diameters and the incorrectness of the number of the fibres used to calculate the stresses. The mean values of the fracture stress and the fracture strain are about 170 MPa and 0.3, respectively. These values are higher than the results reported by Work [5] and Cunniff *et al.* [6]. The elastic modulus of the fibres is about 10 GPa, which is comparable to their results. These values may exceed or may be comparable with the strength of the best man-made fibres, such as aramid fibres.

3.3. Deformation of the capture thread

The solid line in Fig. 6 shows the load(P)–draw ratio (λ) curve for the capture thread taken from the orb-webs. The broken curve is that obtained when the same thread is contracted to half the original length and is pulled again, as described later. It was found that (1) the curve is upwardly concave (J-shaped) and the elastic modulus increases with increase in draw ratio, and (2) although the tensile fracture load is considerably lower than that of the dragline, the fracture strain is higher than 200% which is extremely higher than that of the dragline. As pointed out by Calvert [15], these values may result from one of several possibilities, that (1) the capture thread is swollen and plasticized by a viscid liquid in an amorphous structure, though its composition is the same as the dragline, (2) it has a composition different from that of the dragline, and (3) it has an irregular structure, differing in degree of crystallinity and with a lower orientation than the dragline. Further work to elucidate why the capture thread is much softer and more ductile than the dragline will be needed.

If the capture thread is contracted to less than half its original length, L_0, and is left as it is for a while, the thread kinks, probably due to the surface tension of the viscid liquid; two adjacent droplets distributed along the fibre become closer and coalesce, and subsequently the slack fibre is folded into the coalesced droplets until it becomes tight, as shown in Fig. 7 (1), (2) and (3). When further contracted, a small droplet adjacent to the large one coalesces with the much larger droplet ((4) and (5) in Fig. 7). A larger droplet was carefully placed between two glass slides and observed by optical microscopy. Fig. 8 shows the inside of the glue droplet. It clearly indicates that the loose fibre is folded over several times in the large droplet.

If the sample is pulled again, the fibre which is folded over several times inside the droplets uncoils and is gradually drawn out from the large viscid droplet. The fibre lengthens only in the viscinity of the large droplet, while the other parts are not elongated

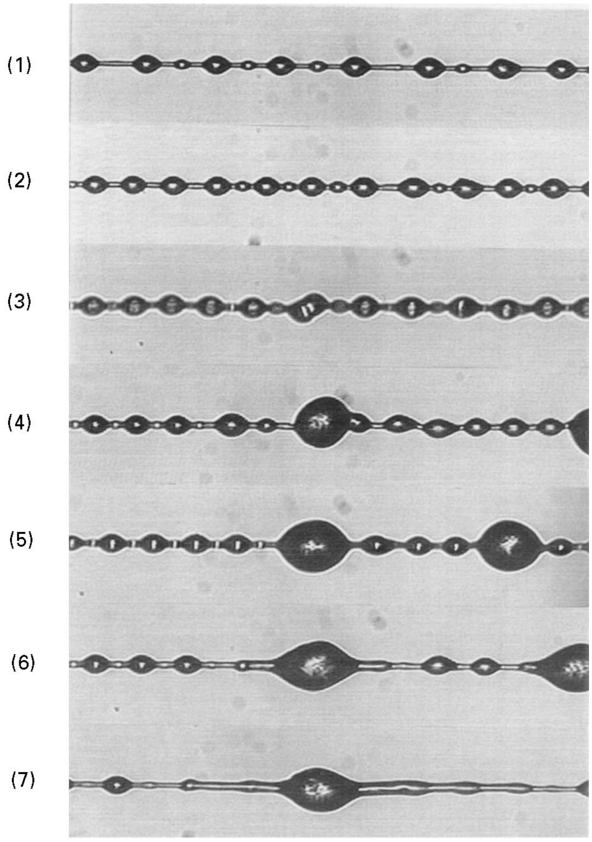


Figure 7 The windlass system of the capture thread. The capture thread (1) is contracted to half the original gauge length (2), the two adjacent droplets coalesce (3), two or three droplets coalesce to a larger droplet 4 and 5; when the thread is pulled again, the folded thread in the droplet is gradually drawn out 6 and 7.

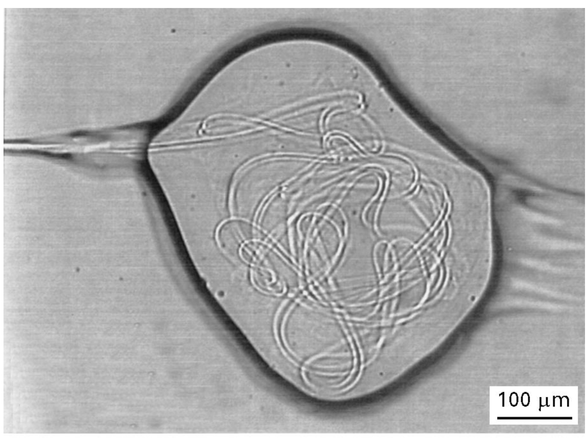


Figure 8 Capture thread folded inside the large droplet. The coalesced droplet laid on to a glass slide was observed through an optical microscope

((6) and (7) in Fig. 7). The resistance encountered when the fibre is pulled out from a viscous liquid may cause the force required for this process. This force is very small until the folded thread in the droplet is completely drawn out and the fibre length is recovered to the original length, L_0. In excess of L_0, the force increases sharply with increasing λ and the P–λ curve becomes J-shaped, tracing the initial curve shown by the broken line in Fig. 6. When the fibre is unloaded and contracted to less than L_0, it is the same droplets

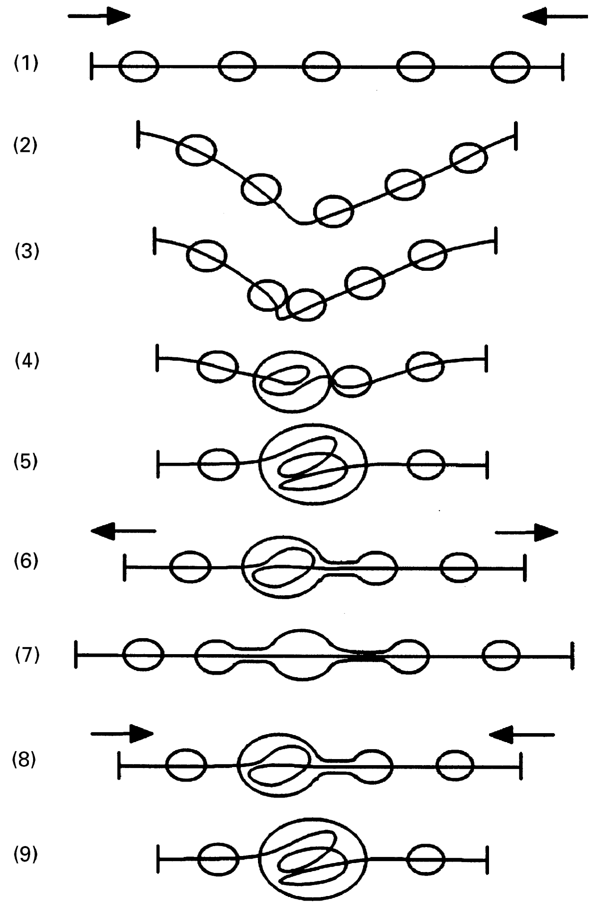


Figure 9 Schematic illustration of the windlass system of the capture thread. The capture thread is contracted to half the original length (1, 2), the thread kinks due to surface tension of the droplet and the adjacent droplets coalesce (3, 4), the thread is folded over several times inside the coalesced droplet (5); when the thread is pulled again, the folded thread is drawn out from the droplet (6, 7), and when the thread is recontracted, the same process as shown above is repeated (8, 9).

which again coalesce as in the previous stage, while the fibre is kept tight. These processes are repeated whenever the droplets coalesce. A schematic illustration of this mechanism is shown in Fig. 9.

Vollrath and Edmonds [16] who were the first to notice this interesting mechanism, termed it the "windlass system". This system may be available when the orb-web is heavily deflected by the collision of flying insects, and the web subsequently recovers its original tight shape.

3.4. Degradation due to UV irradiation

Fig. 10 shows the load–strain curves for the draglines exposed to UV for different times. These samples, as denoted, were taken from the spider collected in October. The strain, ε_f, at fracture decreases sharply with an increase in UV irradiation time. For the sample exposed for 1 day, the strain, ε_f, is only about 5% which is much smaller than the value about 25% for the virgin fibre. The fracture strains as a function of UV irradiation times, t_u, are plotted for the spiders collected at different dates from July to October, in Fig. 11. If the irradiation time exceeds 1 h,

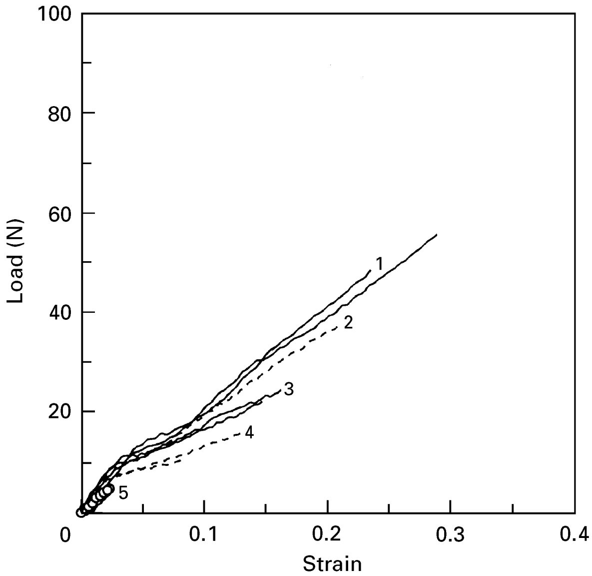


Figure 10 Load–strain curves of draglines irradiated by UV light for different periods: 1 (——) as-spun; 2 (– – –) 2 h; 3 (——) 5 h; 4 (– – –) 10 h; 5 (○ ○ ○) 1 day.

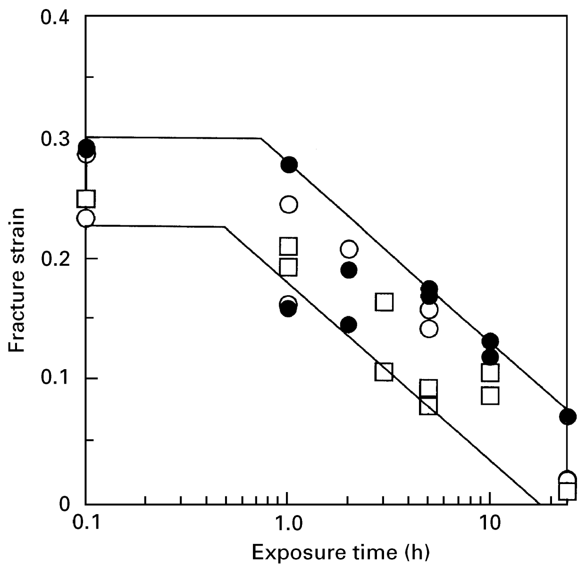


Figure 11 Fracture strain as a function of UV irradiation time for draglines taken at different dates: (●) August, (□) September, (○) October.

degradation begins to occur and its degree increases with increasing t_u.

The dynamic mechanical properties for both the virgin and the UV-irradiated fibres are shown in Fig. 12. The strain variation with an increase in temperature during the test are also denoted in the figure. The results for the (——) virgin and the (– – –) UV-irradiated fibres, are shown. Because they are measured using a bundle of fibres and the cross-sectional area is not obtained exactly, the modulus data are normalized at a reference temperature of 20 °C. The transition near 200 °C, which may be associated with a segmental motion of the main molecular chain, is not very different between the virgin and the UV-

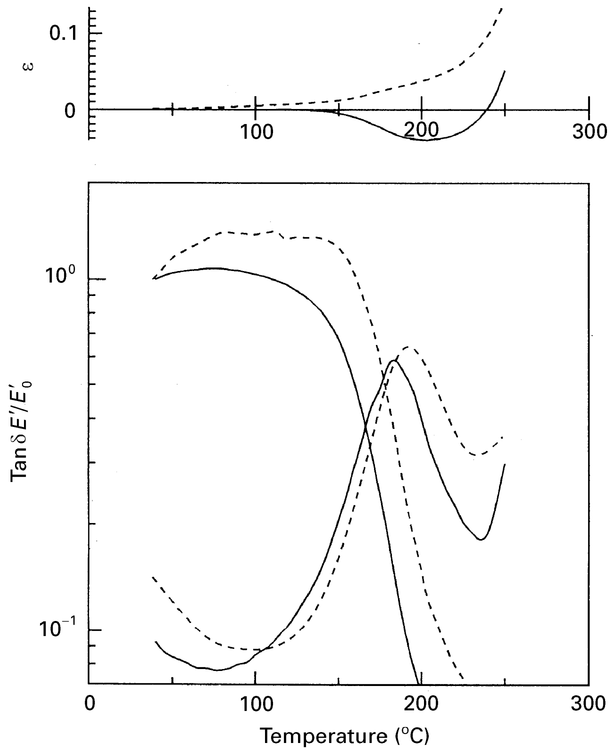


Figure 12 Dynamic properties of draglines (——) as-spun and (– – –) irradiated by UV light, for 1 day.

irradiated fibres. However, the pattern of the strain change is very different between both fibres. In the virgin fibres, the strain decreases once near 150 °C and increases again above ~200 °C with an increase in temperature. On the other hand, for the UV-irradiated fibres, the strain increases monotonically. This monotonic increase is probably caused by initiation of the scission of the intermolecular bond in a large portion of the fibres due to the UV irradiation, and the force caused by the rubber elasticity becoming too small to recover the fibre to the original length. This may provide indirect evidence for scission of the intermolecular bonds of the fibres subjected to UV irradiation.

The draglines exposed to UV irradiation were examined by SEM. No apparent gross defects were noted on their surface. But as shown in Fig. 13, the fracture surface of the UV-irradiated fibre (a), is brittle with no necking and is similar to that broken in liquid nitrogen (see Fig. 2c), while the fibre broken at room temperature (b), is ductile with a swollen aspect near the fracture surface.

The solar energy irradiation to which the earth is subjected in a year is estimated to be about 4500 $MJ\,m^{-2}$ and the UV energy in a wavelength range of 300–400 nm is about 350 $MJ\,m^{-2}$, which is only about 0.07 of the total energy [17]. The UV-irradiation energy in 1 day is nearly equal to 1 $MJ\,m^{-2}$, which may correspond to the energy irradiated during 3 h by use of the present UV generator. This may indicate that the spider thread degrades when exposed to sunlight for 1 day and becomes too brittle to capture large insects, therefore, it is necessary for the spider to renew the orb-web daily.

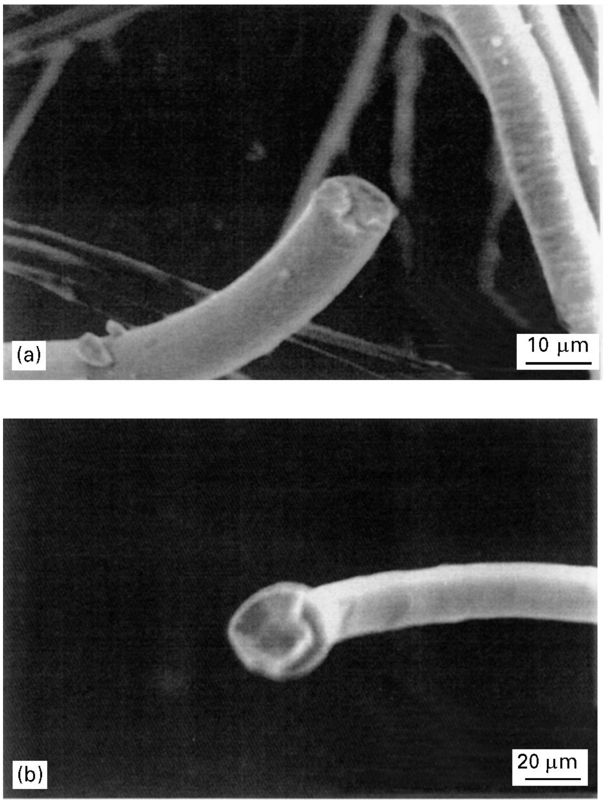


Figure 13 Fracture morphology of dragline (a) irradiated by UV light and (b) as spun.

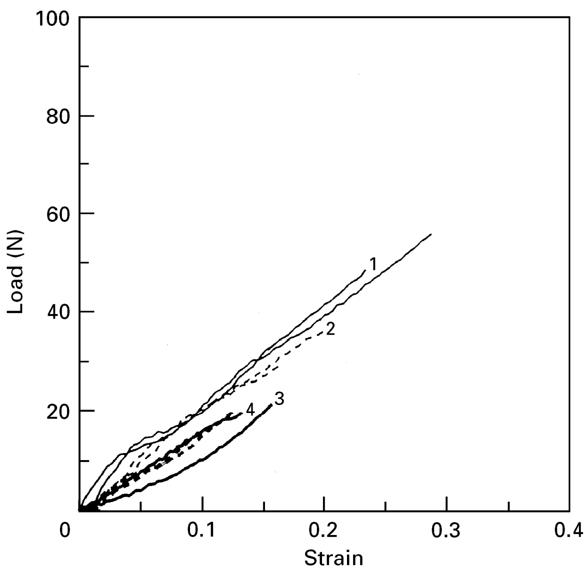


Figure 14 Load–strain curves of draglines wetted by quasi-acid rain for different periods: 1 (——) as-spun; 2 (– – –) 1 h; 3 (——) 1 day; 4 (– – –) 7 days.

3.5. Effect of acid rain

Fig. 14 shows the load–strain curves for the draglines wetted by quasi-acid rain with an acidity of pH 1 during different periods. The draglines were taken from the spiders in October. The fracture strains are expressed in Fig. 15 as a function of the period of exposure to the quasi-acid rain. In acid rain with a strong acidity, the fracture strain decreases with increase in exposure time, t_a. But acid rain with an acidity lower than pH 4 may not cause so much degradation. No change of the smooth surface was observed for the wetted draglines. Considering these facts together, we may conclude that acid rain with an acidity weaker than or equal to that present on earth at the moment, causes no degradation.

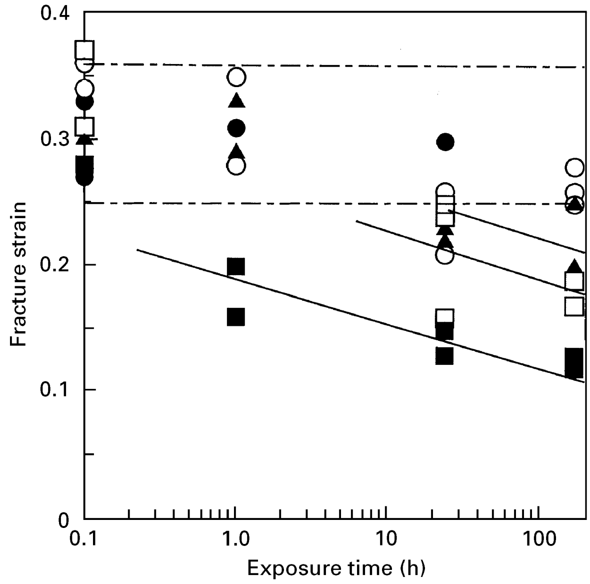


Figure 15 Fracture strain as a function of time wetted by quasi-acid rain of various acidities (pH): (●) 4, (○) 3, (▲) 2, (□) 15, (■) 1.

4. Conclusion

Mechanical properties of spider thread produced by *Nephila clavata* were investigated. It was shown that (1) the dragline consists of microfibrils with a diameter of about 0.1 μm, which is subdivided to amorphous and crystalline regions with size 20–50 nm, whereas its surface is smooth without any characteristic markings, (2) the dragline, which has a fracture stress of about 1500 MPa, a fracture strain of about 0.3 and an elastic modulus of about 10 GPa, is almost comparable or superior to the best man-made fibres such as aramid fibres, (3) the load–strain curve for the capture thread is J-shaped and the fracture strain amounts to about 300%, (4) a series of droplets is regularly spaced along the capture thread, and their coalescence causes a wonderful mechanism termed the "windlass system" by Vollrath and Edmonds, for the extension and contraction of the thread, and finally (5) the irradiation by ultraviolet rays and exposure to acid rain promote the degradation of the dragline.

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References

1. J. M. GOSLINE, M. E. DEMONT and M. DENNY, *Euro-article* **10** (1986) 37.
2. M. YOSHIKURA, "The Biology of Spiders" Gakkai shuppan Center, Tokyo 1987 (in Japanese).
3. M. DENNY, *J. Exp. Biol.* **65** (1976) 483.
4. R. W. WORK, *Textile Res. J.* **46** (1976) 485.
5. *Idem, ibid.* **47** (1977) 650
6. P. M. CUNNIF, S. A. FOSSEY, M. A. AUERBACH and J. W. SONG, in "Silk Polymers: Materials Science and Bio-technology", ACS Symposium series, American Chemical Society, Washington, 544 (1993).
7. M. KITAGAWA, H. SASAGAWA and T. KITAYAMA, *J. Soc Mater. Sci. Jpn.* **44** (1995) 153.
8. M. KITAGAWA, H. SASAGAWA and M. KAWAGOE, *ibid.* **45** (1995) 1445.
9. D. V. MAHONEY, D. L. VESIE, R. K. EBY, W. W. ADAMS and D. L. KAPLAN, in "Silk Polymers: Material Science and Biotechnology", ACS Symposium series, American Chemical Society, Washington, 544 (1993).
10. M. A. BECKER, D. V. MAHONEY, P. G. LENHERT, R. K. EBY, D. L. KAPLAN and W. W. ADAMS, in "Silk Polymers: Material Science and Biotechnology", ACS Symposium series, American Chemical Society, Washington, 544 (1993).
11. S. J. LOMBARDI and D. L. KAPLAN, *J. Arachnol.* **18** (1990) 297
12. K. KERKAM, C. VINEY, D. L. KAPLAN and S. LOMBARDI, *Nature* **349** (1991) 596.
13. K. MURANO, " Acid rain and acid mist" (Shoukabou, Tokyo 1993) (in Japanese).
14. J. HOJOU, " Structure of silkworm silk" (Department of Textile Engineering, Tokyo 1980) (in Japanese).
15. P. CALVERT, *Nature* **340** (1989) 266
16. F. VOLLRATH and D. EDMONDS, *ibid.* **340** (1989) 305.
17. J. HAYAKAWA, "Life and its prediction of high polymers" (I.P.C., Tokyo 1989) (in Japanese).

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