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Ultra-microindentation at the surface of silk membranes

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Abstract

Ultra-microindentation was used to measure the microhardness and modulus of silk (*Bombyx mori*) membranes, cast from 20 to 80 °C. The microhardness and modulus were determined from the loading/unloading curves. The membranes exhibit microhardness of about 400 MPa which is larger than the values for most common synthetic polymers (50–300 MPa) implying a greater scratch resistance. The moduli are of the order of those measured by the other means for *B. mori* silk membranes (5 GPa), and fibers (7–11 GPa). There is some correlation between microhardness and the dimensions of the grains/nanofibrils, but none with surface roughness. The results extend the range of an empirical correlation between microhardness and modulus. The present data together with previous data from other polymers fit the equation, $H = 0.55\,E^{0.74}$, with a correlation coefficient of 0.94. Finally, it is shown that elastic recovery of the silk membranes is an increasing function of the maximum load applied.

Keywords: Ultra-microindentation; *B. mori*; Silk

1. Introduction

In a preceding study, the influence of processing temperature on the morphology of silk membranes was reported [1]. The aim of this note is to examine the influence of the resulting morphology on the micromechanical properties of the membranes. Indentation with a sharp indenter, involving deformation on a sub-micron scale is a convenient way to measure the mechanical properties of materials [2–4]. We have previously used the ultra-microindentation microhardness technique to evaluate the plastic, elastic and flow properties of polymers [5,6].

This note presents new measurements of the microhardness and elastic modulus of silk membranes, cast at different temperatures. Results are discussed in the light of the morphological features of the membranes highlighting the empirical correlation found between microhardness and elastic modulus [7].

2. Experimental

2.1. Materials

The liquid fibroin samples were taken from the middle section of the Middle Division of the silk gland of mature silkworms of *Bombyx mori* one day before spinning. The sericin was removed by washing thoroughly under de-ionized running water. Aqueous solutions of fibroin were prepared by dispersing silk gel in nanopure water. The solutions were then decanted and filtered. Membranes were formed by casting solutions of about 0.35 wt% onto glass plates and annealing/drying at 20, 40, 60, or 80 °C in contact with air [1].

2.2. Indentation procedure

The microhardness of the membranes was measured using a Shimadzu dynamic ultra-microhardness tester. A Vickers square-faced diamond pyramid, with included angles of 136° between non-adjacent faces, fitted to the microscope revolver was used. The samples, prepared in the form of $5 \times 5\ mm^2$ plates, were glued onto a metallic surface for indentation measurements at 21–22 °C and

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45–50% RH. The test parameters were selected using a computer. Table 1 summarizes the experimental values used. The diamond tip approaches the surface at a defined speed. When the indenter contacts the specimen surface, there is a slight load increase that is registered by the control processor. The processor continuously records simultaneously, both, the applied load and the penetration depth. The minimum load applicable is 0.1 mN with an accuracy of 1% and a depth resolution of ± 1 nm.

Fig. 1 shows the loading–hold–unloading cycle obtained using an ultra-microhardness tester operating in the ramp mode and the corresponding contact geometry. The load is incremented at constant speed up to the maximum load (P_{max}), held thereafter for a period of time (Δt), and subsequently released at the same rate as in the loading cycle. The small holding time is used to minimize the creep effect at P_{max}. Continuous depth-sensing recording does not give values of absolute microhardness directly. This is so because the area of indentation is not measured explicitly. However, the loading /unloading data can be processed on the basis of well-established assumptions to yield microhardness and Young's modulus values [8]. This approach considers that the on-load maximum indentation depth (h_{max}) is the sum of the plastic (h_p) and the elastic (h_e) components of indentation. It is further assumed that the area of contact between the indenter and specimen is determined by the plastic deformation only. The value of h_p is then calculated from the analysis of the unloading curve and used to derive the contact depth (h_c). For a Vickers indenter, $A = 24.5h_c^2$, where A is the projected area of indentation. The hardness values were derived from:

$$H = \frac{P_{max}}{A} \quad (1)$$

where P_{max} is the maximum load applied. The elastic modulus, E, was calculated from the initial unloading slope according to:

$$E = \left(\frac{\pi}{A}\right)^{1/2} \frac{S}{2} \quad (2)$$

where $S = \Delta P/\Delta h$ is the initial unloading stiffness.

2.3. Surface characterization

A TopoMetrix Atomic Force Microscope (AFM) was used in the repulsive contact mode at ambient conditions to characterize the surface morphology of the membranes as described previously [1]. The arithmetic roughness (R_a) was determined from 5 μm × 5 μm images obtained previously [1] using the software of the AFM system to analyze 25 to 45 images for each sample. The results for the silk membrane cast at 20 °C were obtained by extrapolation from larger images.

Table 1
Experimental parameter values

Cast temperature (°C)	P_{max} (mN)	dP/dt (mN s^{-1})	t_{load} (s)	Δt_{hold} (s)
20	8	0.8	10	6
40	8	0.8	10	6
60	25	2.5	10	6
80	25	2.5	10	6

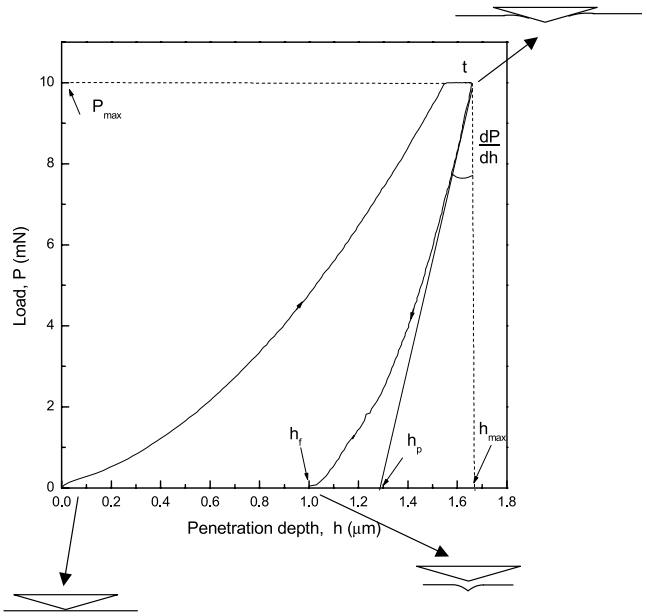

Fig. 1. Loading–hold–unloading cycle obtained using the ultra-microhardness tester operating in the ramp mode.

3. Results and discussion

The experimental data are collected in Table 2. All the indentation values given correspond to an average of data from 15 loading–unloading cycles. For the silk films cast at 20° and 40 °C, P_{max} was 8 mN because of the thinness of the samples (10 and 15 μm, respectively). The ratio between the penetration depth and the sample thickness (δ) always has to be kept below 10% [2] ($h_{max}/\delta \leq 1/10$). Table 2 also

Table 2
Sample thickness (δ), maximum penetration depth (h_{max}), stiffness (S), plastic component of indentation (h_p), derived values of H, E and surface roughness (R_a) obtained for the *B. mori* silk membranes cast at different temperatures. The data given are based on 15 measurements as are the uncertainties which are standard deviations

Casting T (°C)	δ (μm)	h_{max} (μm)	S (mN/μm)	h_p (μm)	H (MPa)	E (GPa)	R_a (nm)
20	10	0.842	52.04	0.688	430 ± 19	10 ± 2	7 ± 7
40	15	0.909	32.49	0.663	337 ± 30	6 ± 2	12 ± 4
60	35	1.500	73.58	1.170	495 ± 25	9 ± 1	17 ± 6
80	40	1.630	70.46	1.271	431 ± 40	8 ± 1	8 ± 7

includes the surface roughness values for the 24 to 45 images of the studied samples.

The microhardness is greater than that for most synthetic polymers suggesting a greater scratch resistance. The measured elastic moduli are of the order of values obtained by other methods for *B. mori* silk membranes (~5 GPa) [9] and fibers (7–11 GPa) [10].

Fig. 2 illustrates the load–displacement curves for the silk membrane sample cast at 80 °C after loading and unloading using four different loads. It is shown that, for the 40 μm-thick sample used, the loading–unloading behavior is independent of the load applied. It also can be seen that the elastic recovery ($h_{max} - h_f$) is increasing with the load applied. This effect is shown in Fig. 3 which shows that the elastic recovery of the silk membranes cast at different temperatures, is an increasing function of the maximum load applied. This correlation covers only a narrow range of P_{max} values. Experiments performed at higher loads are in preparation. Fig. 4(a) shows a plot of microhardness variation with increasing average size of the nanofibrils [1]. The correlation coefficient is 0.8, in support of a correlation between H and nanofibril size. Fig. 4(b) shows the plot of microhardness versus average size of grains [1]. The correlation of 0.5 here is much weaker. Since the correlations in Fig. 4 also might result from the possibility that surface roughness could be the underlying key parameter, the roughness was measured. However, it exhibits no correlation to the microhardness (not shown), thus eliminating the possibility. Fig. 5 shows a double logarithmic plot of microhardness versus elastic modulus including the present data for the silk membranes and other data for different polymers [2,7,11–13]. The straight line yields a correlation coefficient of 0.94 and can be represented by the equation $H = 0.55 \times 10^{0.74}$. Most interesting is the fact that the H and E values for the silk membranes are the highest ones, in all the range of the polymers studied.

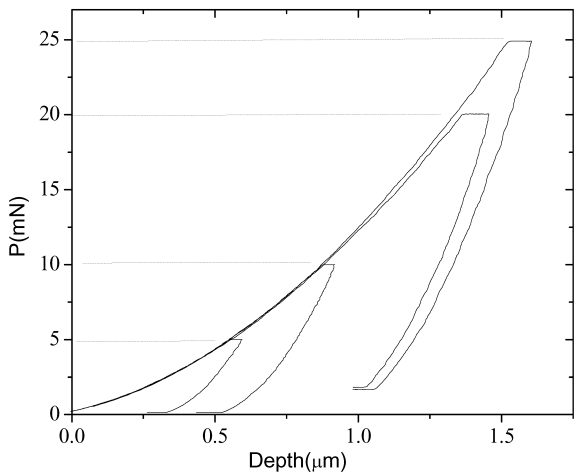

Fig. 2. Typical load–displacement curves for silk membrane cast at 80 °C after loading and unloading using four different loads.

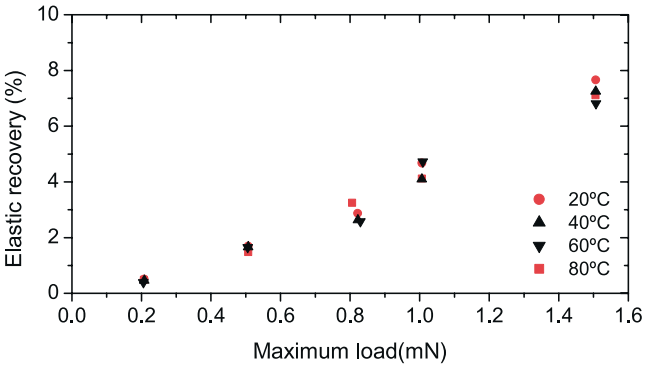

Fig. 3. Elastic recovery of the silk membranes as a function of the maximum load applied.

4. Conclusions

- Thermally treated silk membranes exhibit microhardness values around 400 MPa that are notably larger than those of common synthetic polymers (50–300 MPa) implying a greater scratch resistance.
- The elastic modulus values, derived from the ultra-microindentation test are of the order of results obtained by other methods for *B. mori* silk membranes and fibers.
- The nature of the morphology features (grains, nanofibrils) of the silk membranes seems not to strongly influence the surface microhardness values, but it appears that the microhardness does correlate to some extent with the dimensions of the morphological features.

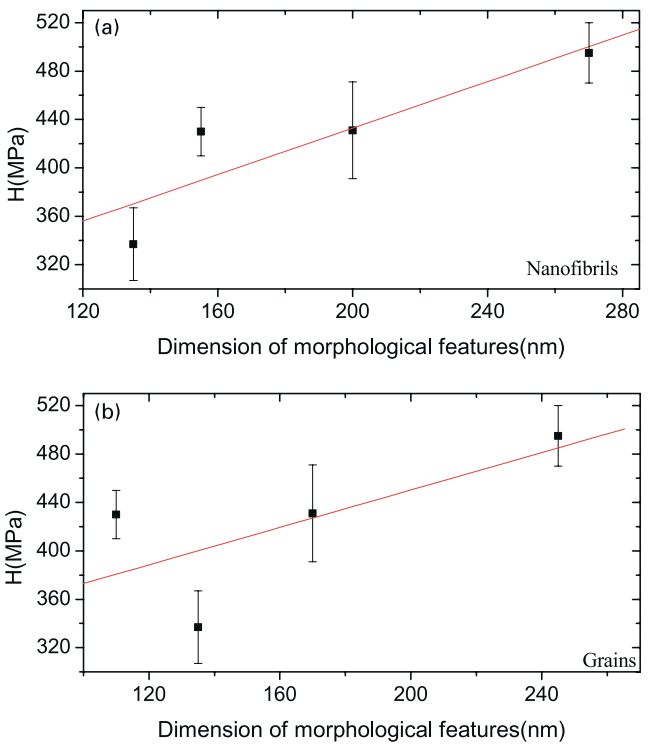

Fig. 4. Plot of microhardness vs. (a) average size of nanofibrils (correlation coefficient 0.8). (b) Average size of grains (correlation coefficient 0.5).

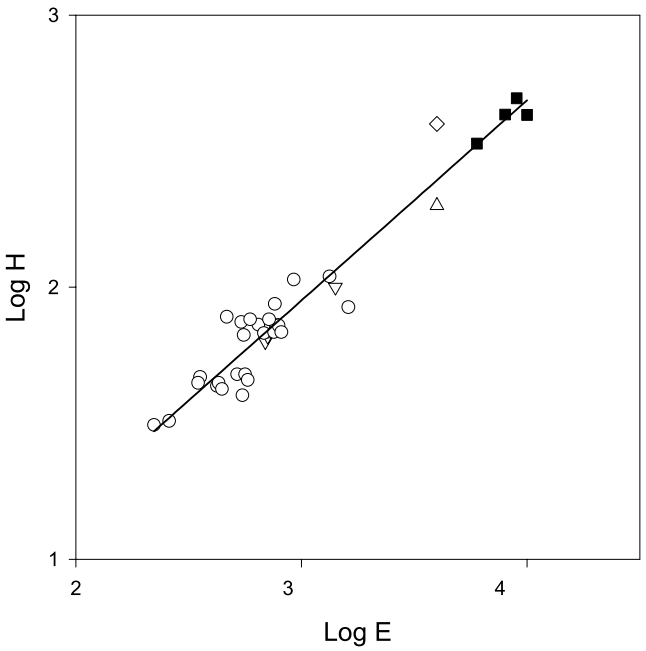

Fig. 5. Log–log plot of microhardness (MPa) vs. modulus (MPa) for a variety of polymers. The data reported here are for ■ silk, ◇ PMMA [11], △ PEEK [11], ▽ PP [12], ○ PE [13], and — $H = 0.55\,E^{0.74}$ (correlation coefficient 0.94).

- The microhardness appears not to correlate with the roughness of the membranes.
- The data extend the range of an empirical correlation between microhardness and modulus of the form $H = 0.55 \times 10^{0.74}$ with a correlation coefficient of 0.94.
- The elastic recovery of the silk membranes is an increasing function of the maximum load applied.

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