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Mechanical properties of silkworm cocoons

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Abstract

Silkworm caterpillars, *Bombyx mori*, construct cocoons in order to protect their moth pupas against possible attacks from the outside. We experimentally measured the mechanical properties (Young's modulus, tensile strength, and thermo-mechanical parameters) of normal compact cocoons and the variations of these properties in the thickness direction of a cocoon. Tension tests were carried out by using rectangular specimens of two types, either cut from a normal compact cocoon or peeled from its different layers, respectively. We found that, on one hand, the overall or thickness-averaged mechanical properties of *B. mori* cocoons are excellent. More interestingly, on the other hand, the elastic modulus, strength and thermo-mechanical parameters all vary along the thickness direction of a cocoon in an apt manner, further enhancing its ability to resist possible attacks from the outside. In addition, the properties of a cocoon show distinct differences in the longitudinal and transverse directions. The relation between the mechanical properties and microstructures is discussed. Finally, the main features of the fracture process of cocoons and silks were also analyzed based on SEM observations. This study was attempted to gain an understanding of the mechanical behaviors and their dependence on the microstructures of cocoons, and it might be also helpful in guiding the design of novel safe-guarding devices and biomimetic materials.

Keywords: Silkworm cocoon; Polymer composite materials; Biomaterials

1. Introduction

Cocoon shells produced by silkworm caterpillars are one kind of natural structures and polymeric composite materials which possess excellent mechanical properties. After eating mulberry leaves almost constantly for 4–6 weeks (in order to store enough nutrient and to be able to shed their skins five times), silkworm larvae start to construct protective cocoons for their pupas. The cocoon protects the moth pupa against microbial degradation and desiccation during metamorphosis, and also protects against potential predators [1,2]. A silkworm caterpillar spins a lightweight and compact cocoon around itself by continuously moving its head in the shape of either a figure 8 or an S and by cyclically bending and stretching its body. The construction of a cocoon needs approximately 3 days. After it has finished spinning the cocoon, the silkworm sheds its skin one last time and becomes a pupa. The silken cocoon shell is comfortable and protective, allowing the pupa in it to evolve into a silkworm moth. The ellipsoidal cocoon has the smallest thickness at its two ends so that the moth can break through it after the metamorphosis from pupa to moth. The cocoon has many wrinkles on its outer surface [3] that form due to non-uniform shrinking during drying. A cocoon is a natural polymeric composite shell made of a single continuous silk strand with a length in the range of 1000–1500 m and conglutinated by sericin. The raw silk comprising the cocoon consists of two proteins, sericin and fibroin. The former is soluble in hot water, while the latter not. Owing to their extraordinary mechanical properties such as Young's modulus and strength, natural silk fibers produced by silkworms, spiders and hornets have attracted extensive attention in the past decade. Studies on the relationship between their macroscopic properties and multiscale micro- and nano-structures seem to be of especially great interest, as a means to design and fabricate advanced biomimetic materials [4–10].

The cocoon is a product of central mechanisms tuned to and tuned by external and internal environments. Both the construction and the formation of cocoons have been

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investigated [11–15]. Van der Kloot and Williams [11–13] studied the spinning process of silkworms under different conditions; for instance, by changing the spinning platform, considering the carbon monoxide and carbondioxide's effect, and varying chemical and surgical procedures. Kaise and co-workers [14,15] suggested some computational models for simulating the movement pattern of a larva head and the stretching, bending and swinging of its body to form a cocoon. Using optoelectronic methods, Musayev [16] examined some technological parameters of cocoons, e.g. spectrum characteristics describing cocoon shell's absorption and reflection of light in various wavelengths. Using thermogravimetry, differential thermal analysis and Fourier transform infrared absorption spectrometry, Zhang et al. [17] studied the color, size, and shape of *Bombyx mori* cocoon shells after heat treatment at increasing temperatures. It was found that the size decreased with an increase in temperature and weight was lost from the cocoon shell. Tsukada et al. [18–21] studied the thermal decomposition behavior of sericin cocoons and structural changes of silk fibers induced by heat treatment.

Cocoon shells play a significant role in the transformation from silkworm and pupa to adult moth. Investigations on the physical and mechanical properties of this kind of natural polymer composite materials will be of particular significance to gain a deeper understanding of the evolution and physiology of silkworms, natural polymer processing system and will be of interest for the biomimetic design of artificial structures. To date, however, there is a surprising lack of research on the mechanical properties and microstructures of silkworm cocoons. The present paper is aimed mainly at systematic experimental investigations of silkworm cocoons, which can be considered as a layered biomaterial bonded by sericin. We studied cocoon shells constructed by Chinese silkworm larvae, *B. mori*. Not only were such properties as the elastic modulus and strength of the cocoon as a composite shell obtained, but their variations along the thickness direction were also measured by skillfully peeling a cocoon into some thinner layers. It is interesting to find that both the elastic modulus and strength vary in the thickness direction in such a manner that a cocoon can bear efficiently both external static forces and dynamic impact loadings. Complete stress–strain curves of rectangular specimens cut from these different cocoons were obtained. Microstructures and fracture modes of cocoons and silks were observed by SEM.

2. Materials and methods

2.1. Materials

The silkworms, *B. mori*, were placed at the end of the fifth larval instar in an environment appropriate for them to spin cocoons. A silkworm constructs a complete cocoon within 60–70 h. The aspect ratio of an ellipsoidal cocoon, defined as the length ratio between the long- and the short-axes, is about 1.8. We measured two types of specimens as follows:

(i) Some rectangular specimens of about 3–3.5 mm in width and 30 mm in length were cut from five intact cocoons along the longitudinal and the transverse directions. Evidently, the thickness of such specimens equals that of a normal compact cocoon and is in the range of 0.3–0.5 mm.

(ii) To measure the variations of mechanical properties in the thickness direction of a cocoon, some rectangular specimens cut from normal compact cocoons were further peeled skillfully into several layers, i.e. specimens with a thickness much smaller than a cocoon. In our experiments, the peeling numbers n of layers were chosen as 2, 4 and 10 for different specimens. The peeling of a compact cocoon was performed using a pair fine-point tweezers under a dissecting microscope. We first measured the thickness of a to-be-peeled rectangular specimen cut from a cocoon and determined the average thickness of the required thin specimens according to the peeling number. Then a sharp scalpel knife was used to cut some small notches as marks of peeling, which were distributed as uniformly as possible along the cross-section at one end of the specimen to guarantee identical thickness in each layer. Finally under the dissecting microscope, we used the tweezers to peel carefully and slowly the specimen into thinner layers having an approximately identical thickness. The peeling of a specimen into 10 layers (i.e. for the largest peeling number we considered) is especially difficult and skillful. Generally, the peeling number cannot be larger than 16 in order to guarantee the integrity of the thin specimens peeled.

2.2. Methods

Quasi-static uniaxial tension tests were performed at room temperature using a computer controlled AGS-10KN Universal test machine to study the deformation and failure behaviors of the cocoons. The crosshead speed was adjusted to obtain a loading rate of 2 mm/min in the specimen gage section of 10 mm in length as measured by an extensometer. The load cell was set at 50 N. The force–displacement curves were recorded by a computer. Due to the possible dispersion in the experimental data, five or six specimens of each type were measured at the same condition to yield an averaged result. In addition, a Shimadzu Corporation model SS-550 SEM was used to observe the microstructures of the specimens before the tension tests and their fracture behaviors after the tests.

Thermo-mechanical properties of the cocoon specimens were also determined with a dynamic thermo-mechanical

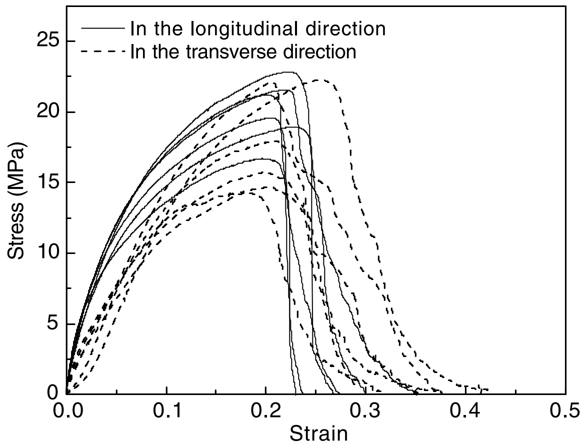

Fig. 1. Typical tensile stress–strain curves of normal compact cocoon.

analyzer (TA instrument DMA 2980-USA). The storage modulus (E'), loss modulus (E''), and the loss factors tan $\delta = E''/E'$ were obtained from uniaxial tension tests. A small static force of 0.01 N was applied along the axial direction of the sample. The displacement amplitude was set as 20 μm. The measurements were performed at a frequency of 1 Hz with a temperature range from 35 to 320 °C.

3. Results and discussions

3.1. Mechanical properties of normal compact cocoons

Quasi-static tension tests were first performed for rectangular specimens cut from normal compact cocoons along the longitudinal and the transverse directions. Some representative tensile stress–strain curves from the same cocoon are given in Fig. 1. The measured tensile moduli and strengths and their standard deviations of a representative cocoon are listed in Table 1, where the serial number is defined from the outside to the inside. The specimen group numbers I–IV stand for the specimens cut from a normal compact cocoon and the thinner specimens with the peeling number being 2, 4 and 10, respectively. A sufficient cocoons and specimens have been measured, and it was found that the results can be reproduced well.

The normal compact cocoon exhibits a high ability of elastic deformation, with an elastic limit strain higher than 20% in both the longitudinal and the transverse directions. The elastic deformation exhibits an evident non-linearity, especially at higher strains. Both the Young's modulus and the tensile strength of a cocoon in the longitudinal direction are higher than those in the transverse direction, as given in Table 1. It is found that the Young's modulus and tensile strength in the longitudinal direction are 1.3–2.1 and 1–1.3 times those in the transverse direction, respectively. However, the elongation ratio (or the ultimate fracture strain) in the transverse direction is about 1–1.3 times that of the longitudinal direction. It will be shown in Section 3.2 that the properties of a normal compact cocoon are heterogeneous in the thickness direction, and the above measured data represent the macroscopically averaged mechanical properties over the entire thickness of a normal compact cocoon. The anisotropic properties of cocoons are attributed mainly to the non-uniform distribution of orientations of silk segments.

It is interesting to note that the differences in both the Young's modulus and the tensile strength in the two directions are not accidental but requisite for a cocoon to provide an efficient protection to the moth pupa. It is well

Table 1
Mean tensile modulus, ultimate tensile strength and their standard deviations of complete cocoon, two, four and 10 peeled layers

Specimen group number	Serial number of the layers	Mean tensile modulus and standard deviations (MPa)	Mean ultimate tensile strength and standard deviations (MPa)
No. I	Longitudinal direction	337 ± 50.6	20.1 ± 2.18
	Transverse direction	170 ± 21.1	17.8 ± 3.61
No. II	1st	196 ± 29.8	17.9 ± 2.72
	2nd	362 ± 50.6	27.1 ± 3.40
No. III	1st	134 ± 17.1	10.1 ± 1.35
	2nd	269 ± 57.3	18.3 ± 2.28
	3rd	272 ± 44.7	15.6 ± 3.29
	4th	413 ± 24.7	28.6 ± 3.84
No. IV	1st	181 ± 28.3	6.8 ± 0.34
	2nd	292 ± 81.5	3.1 ± 1.21
	3rd	315 ± 68.1	6.4 ± 1.01
	4th	314 ± 53.8	6.7 ± 2.71
	5th	228 ± 59.3	14.3 ± 1.71
	6th	235 ± 41.9	19.4 ± 0.74
	7th	293 ± 64.8	5.8 ± 1.72
	8th	259 ± 107.1	18.5 ± 3.43
	9th	331 ± 29.1	24.0 ± 4.06
	10th	449 ± 108.0	35.1 ± 5.87

For the thinner specimens, only the measured data along the longitudinal direction are given.

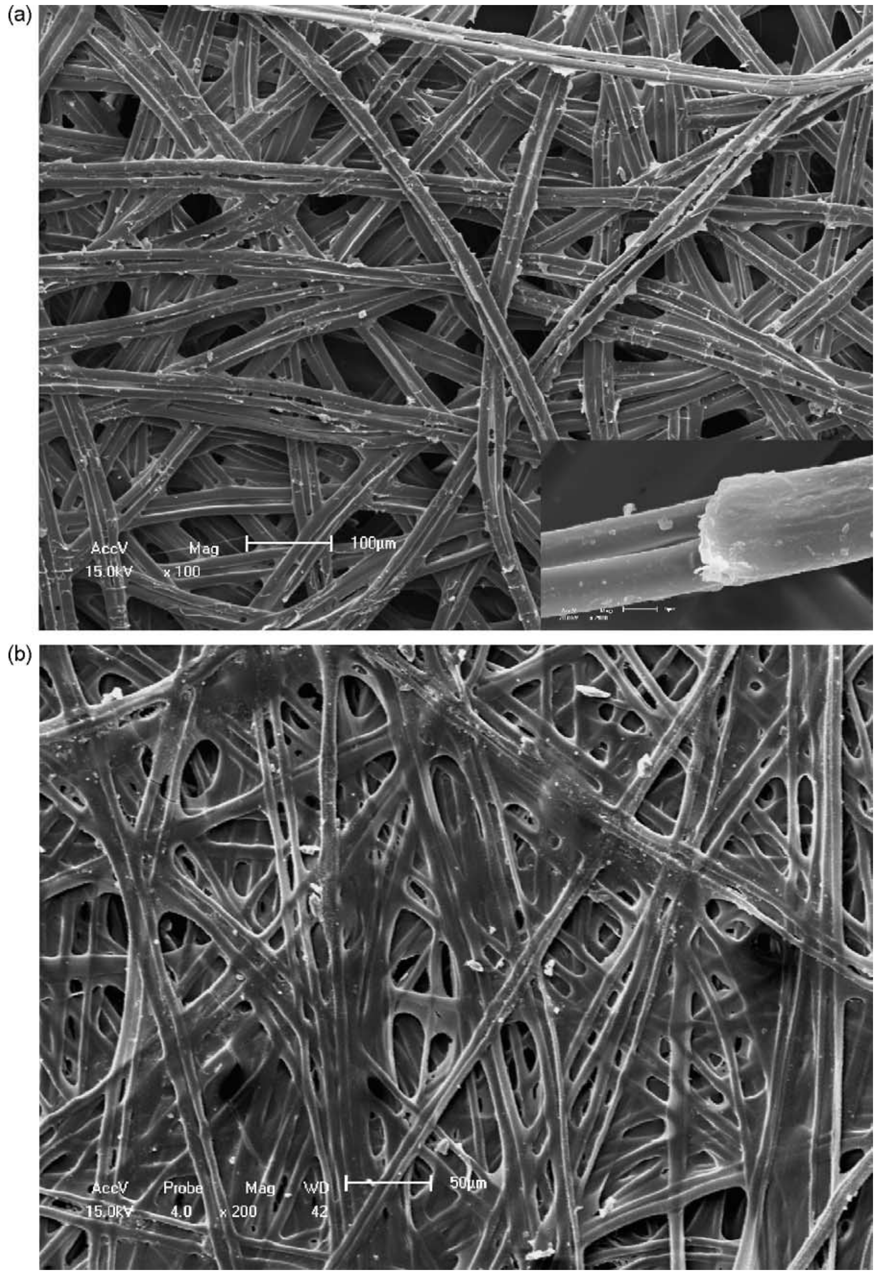

Fig. 2. SEM images of the microstructure of a cocoon: (a) The outermost layer and (b) the innermost layer. The inset in (a) shows the fibroin-sericin structure of the silk (scale bar = 5μm).

known that in order to resist the same applied force without an occurrence of rupture and large deformation, both a higher Young's modulus and a higher strength are required for a longer beam (corresponding to the longer axis) than for a shorter one (corresponding to the shorter axis). For a cocoon comprised of a single long silk bonded by sericin (like those considered in the present experiments), the anisotropic elastic properties and strengths depend mainly upon the microstructures and silk orientations in it. Therefore, a silkworm caterpillar makes an anisotropic microstructure of the cocoon by controlling the movement paths of its head and body in order to achieve an optimum orientation distribution of silk and the superior mechanical properties using the limited raw material within its body.

Two SEM images of the microstructure of the outermost and the innermost layers of a normal compact cocoon are given in Fig. 2(a) and (b), respectively. It can be seen from the inset of Fig. 2(a) that the silk produced by the silkworm actually consists of two threads bonded by sericin, spun from silk glands. It is seen from Fig. 2 that the inner layer has a lower porosity (i.e. a higher silk density) and a smaller average diameter of silk than the outer layer, yielding an increase in the elastic modulus and strength from the outside

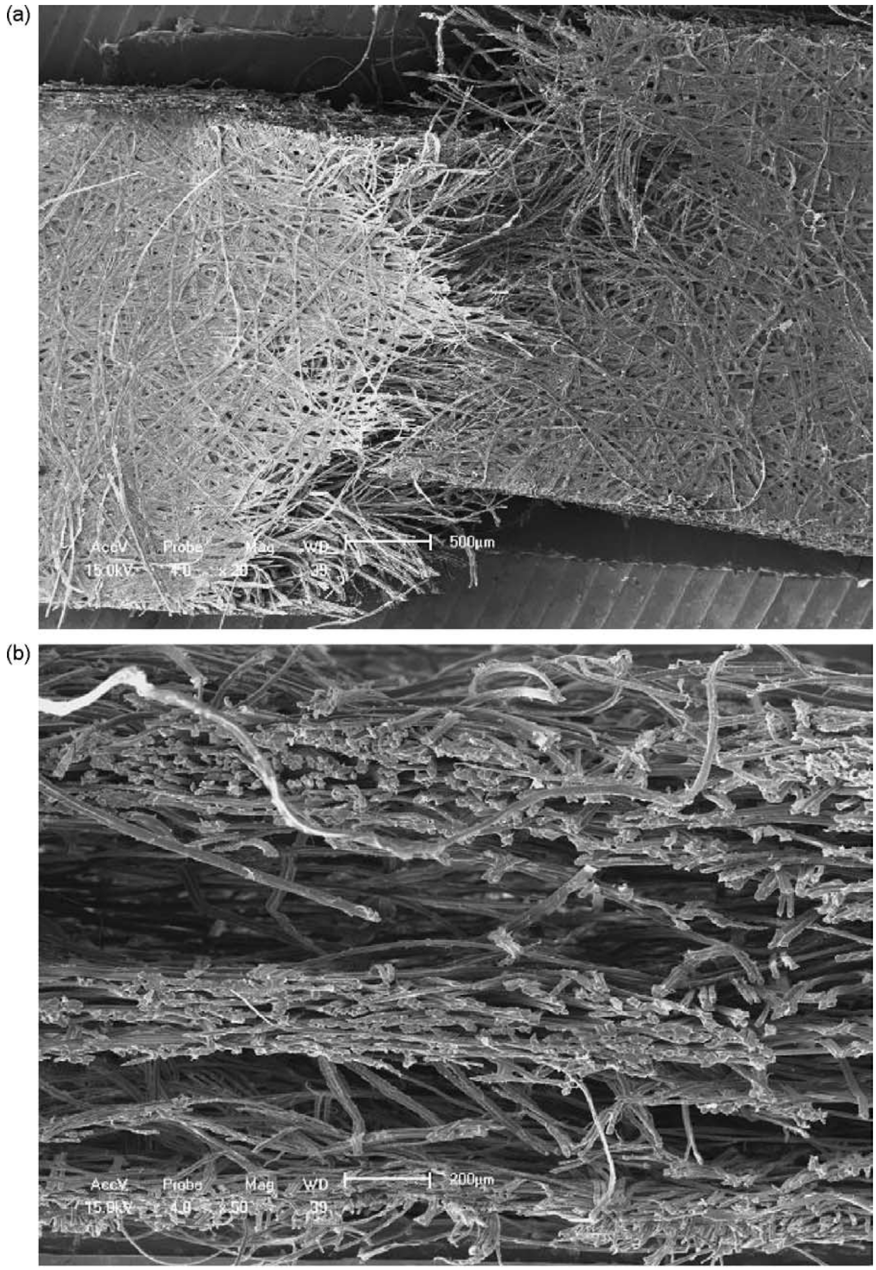

Fig. 3. SEM images showing the failure mechanisms of a cocoon under tension: (a) Fracture pattern and (b) delamination of sub-layers.

to the inside. However, the exact measurement of the change in the porosity along the thickness direction is difficult. The cocoon may be considered as a fiber network of bestrewed cavities [22]. Such a porous thin shell structure plays a significant role in the evolution of silkworms. It is an optimal structure, which uses a limited amount of raw materials (silk made of sericin and fibroin) to achieve a superior ability against possible attacks from the outside. The SEM image in Fig. 3(a) shows a typical fracture pattern of the compact cocoon specimens. During tension, delaminations of the sub-layers occur in the thickness directions due to the relatively weak bonding of sericin, as shown in Fig. 3(b).

3.2. Variation of mechanical property in the thickness direction

There seems to be no report in the previous literature on the variation of such mechanical properties as the elastic modulus and the strength of a cocoon in its thickness direction. To this end, we carefully split a specimen cut from a normal compact cocoon along the longitudinal direction into two, four or 10 layers, as described in Section 2.1. Some representative stress–strain curves of such split specimens are shown in Fig. 4(a)–(c), corresponding to $n=$ 2, 4 and 10, respectively. The average Young's moduli and tensile strengths of the different specimens and their

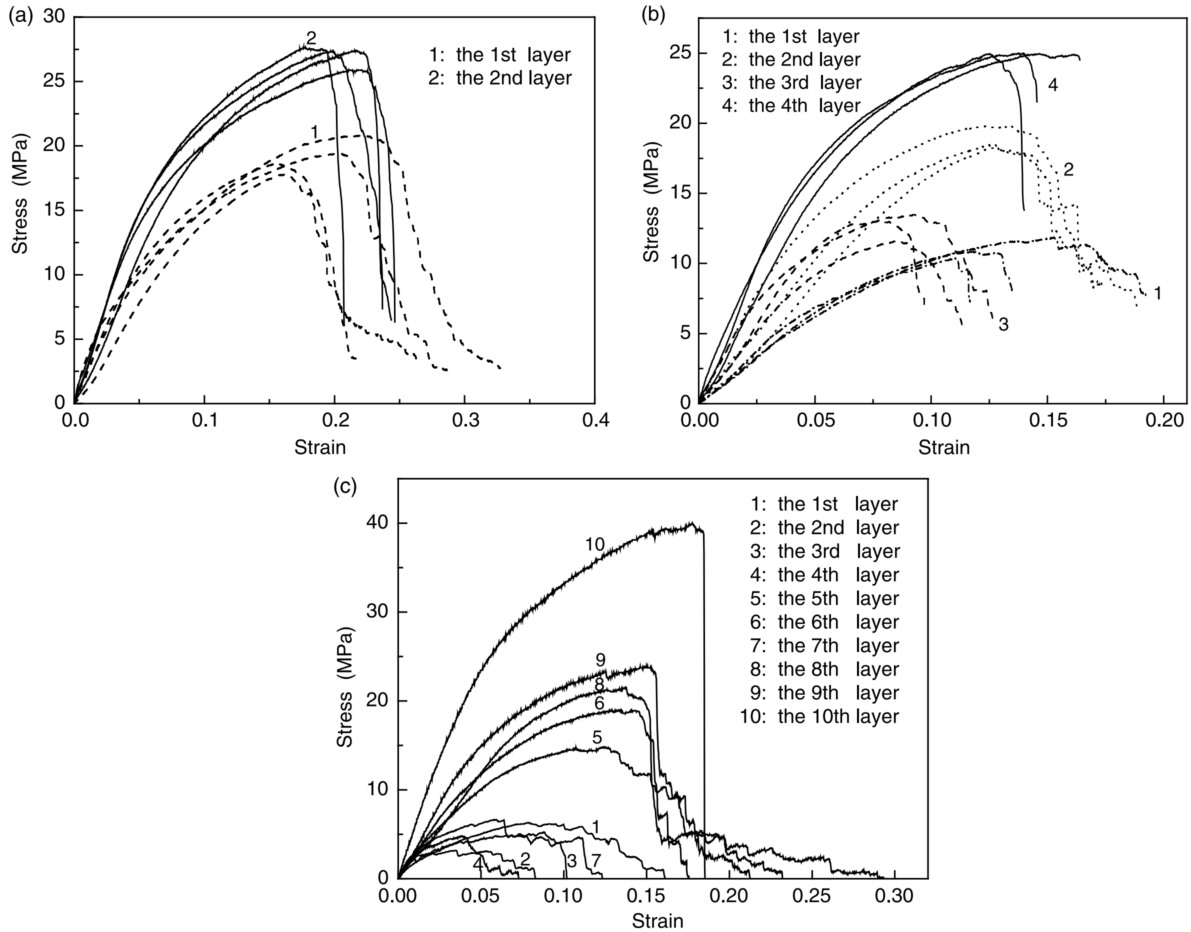

Fig. 4. Tensile stress–strain curves of different layers of a cocoon: (a) $n=2$, (b) $n=4$, and (c) $n=10$. The serial numbers stand for the different layers from the outer to the inner of the normal compact cocoon.

standard deviations are given in Fig. 5 and Table 1. It is obvious from Figs. 4 and 5 that both the elastic modulus and the strength increase from the outside towards the inside as a whole, and have the maximum values at the innermost layer. Such a functionally gradient variation of mechanical properties leads to a very good, if not the best, ability for cocoons to bear forces from the outside. Most possible dangers and attacks to cocoons are from the outside. Therefore, the maximum tensile stresses happen always at the innermost layer. Through the evolution of millions of years, therefore, an optimized microstructure has formed to efficiently resist possible impacts. The higher elastic modulus and strength of the inner layers result from two mechanisms of microstructure. One is due to the more dense silk distribution and the lower porosity in the inner layers (Fig. 2), and the other is due to the fact that the silk in the inner layers is generally thinner in diameter, as has been measured from our experiments. Our experimental measurements also showed that the thinner the silk, the higher the elastic modulus and tensile strength.

Generally, a multilayered structure has a better energy-absorbed property than a homogeneous one due to the wave-impedance matching of different plies [23–25]. The increase in the elastic modulus and the strength from the outside towards the inside are especially efficient in resisting against dynamic and impact loading. Therefore, the variation of mechanical properties in the thickness direction leads to the superior ability of cocoons to bear both static and dynamic forces and protect the moth pupa.

3.3. Dynamic thermo-mechanical properties

Dynamic mechanical thermal analysis (DMTA) was also performed in order to characterize the mechanical and thermal properties of cocoons. Tensile tests of the different rectangular specimens described in Section 2.1 were carried out using a dynamic thermo-mechanical analyzer to measure the storage (dynamic) modulus E' and the loss (dissipation) modulus E''. Thereby, one can obtain the mechanical loss factor, $\tan \delta = E''/E'$, which stands for the damping performance of a material. Some representative changing curves of E', E'' and $\tan \delta = E''/E'$ with respect to the temperature are given in Fig. 6 for a normal compact cocoon and its four layers.

It can be seen from Fig. 6(a) that with the increase in temperature from 35 to 320 °C, the storage moduli E' of the

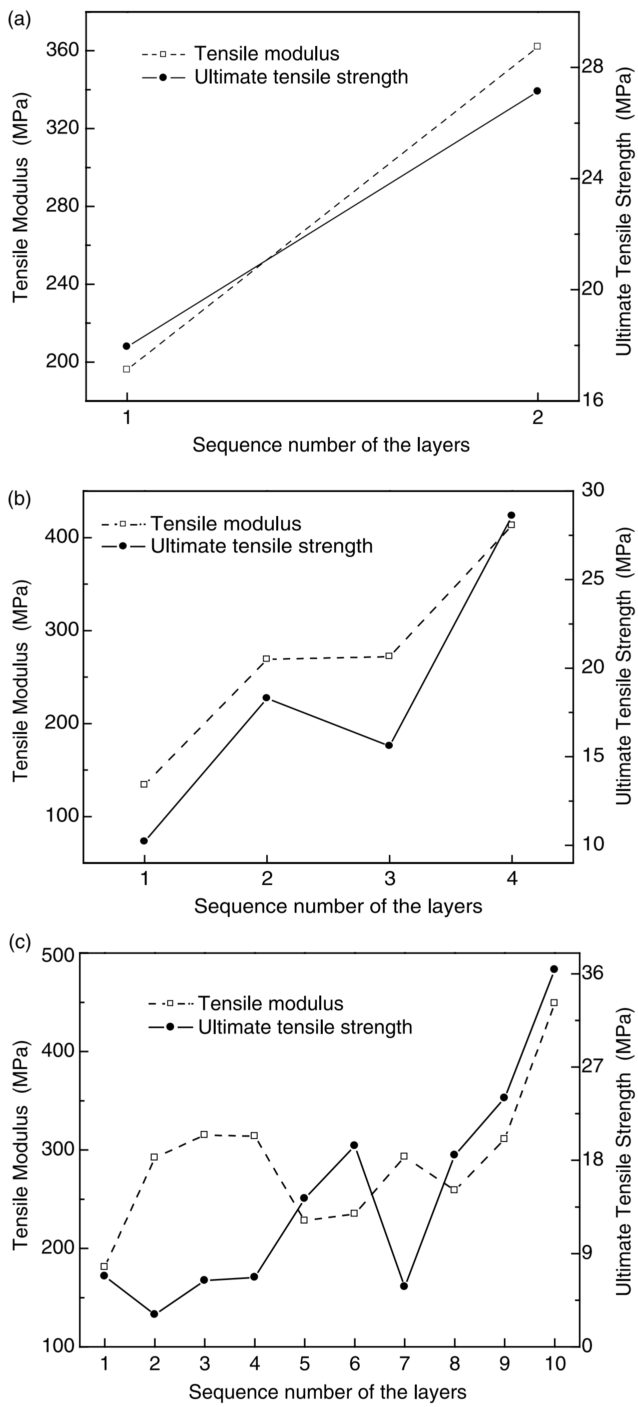

Fig. 5. Variations of Young's modulus and tensile strength in the thickness direction of a cocoon: (a) $n=2$, (b) $n=4$, and (c) $n=10$.

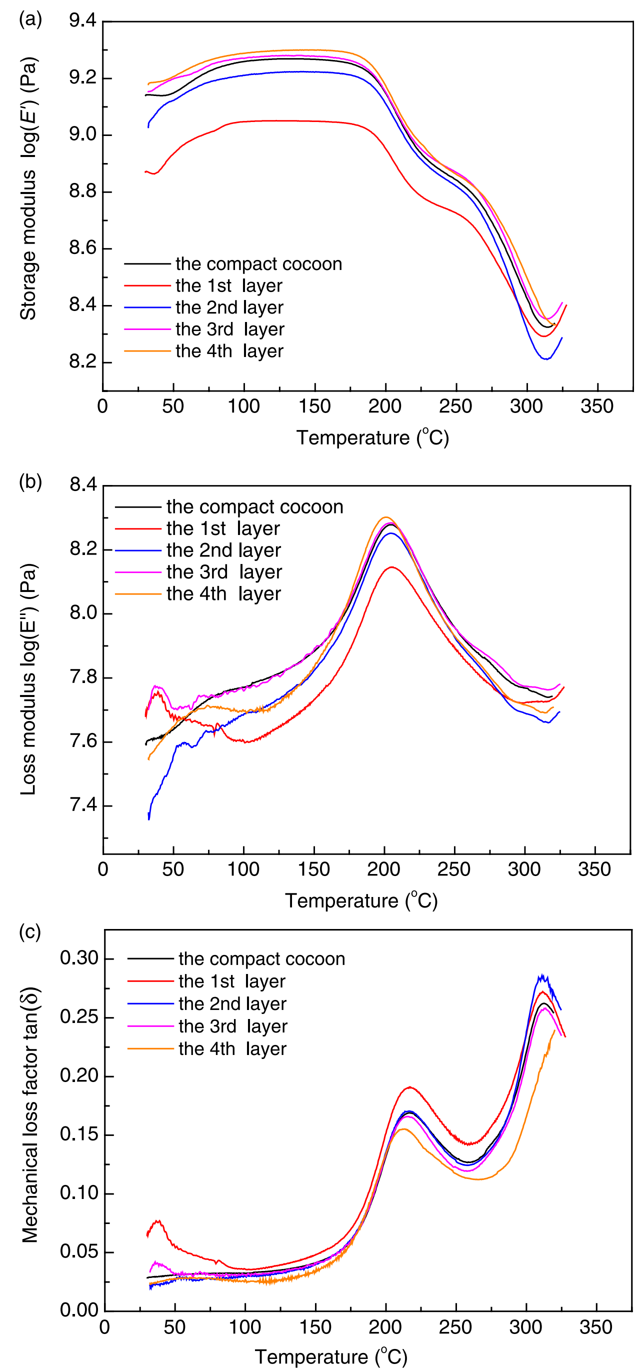

Fig. 6. Dynamic thermo-mechanical properties of a cocoon and its different layers: (a) Dynamic storage moduli, (b) loss moduli and (c) mechanical loss factors.

normal compact cocoon and its different layers all show a slow tendency to increase before reaching their peak values at about 175 °C, and then decrease slowly. Comparatively, the changes of the loss moduli E'' with temperature are faster, as shown in Fig. 6(b). The values of E'' first increase, reach their peaks at the onset temperature around 200 °C, then decrease quickly as the temperature increases until about 270 °C, and finally exhibit another relatively slower increasing stage. The onset temperature, i.e. the endothermic peak of the loss moduli, corresponds to the glass transition temperature (T_g) of the cocoon [26–28]. At a temperature above T_g, the cocoon and its layers become softer and softer and behave similar to a rubber-like material. From Fig. 6(b), it is seen that the glass transition temperature T_g of the normal compact cocoon is 204 ± 1.2 °C, while the T_g values of the four layers from the outside to the inside, designated, respectively, as 1, 2, 3 and

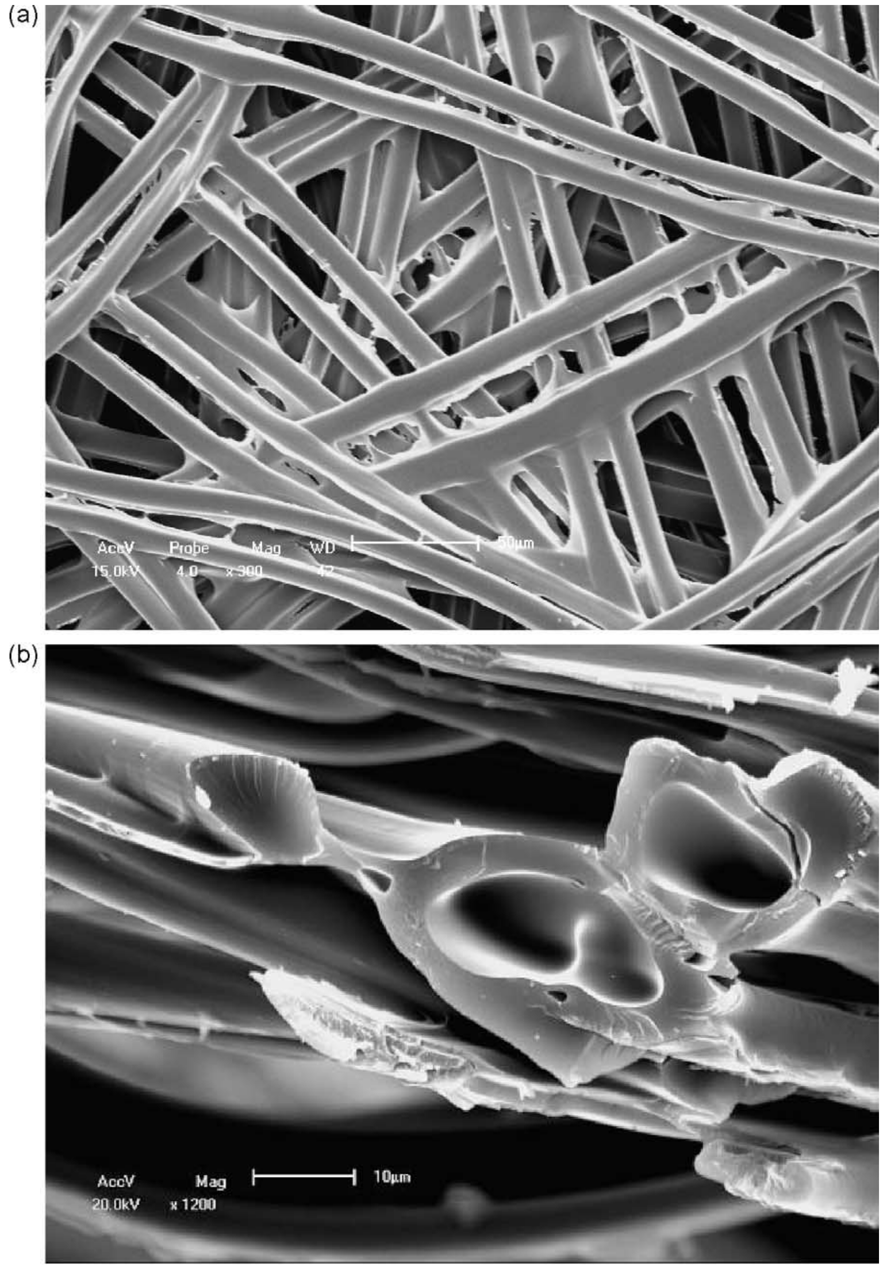

Fig. 7. SEM images of the fracture of a cocoon after DMTA test: (a) Unbinding of two threads of silks, (b) fracture of silks, and (c) crazes on a silk surface.

4, are 208±0.9, 204±1.1, 203±1.3 and 200±0.5 °C, respectively. The T_g value of the cocoon is close to that of the second layer. The shift of the endothermic peak of the loss moduli from the outer layer to the inner is attributed to the change of the volume fractions and the varying crystallization of sericin and fibroin in the silks of different cocoon layers [3]. Tsukada et al. [18–21] reported that the glass transition temperatures of the sericin and fibroin of *B. mori* silks are about 215 and 175 °C, respectively. Our experimental measurements of silks show that from the outside to the inside of the cocoon, the volume fraction of sericin decreases while the relative content of fibroin increases. Therefore, the shifting tendency of the glass transition temperature of the cocoon we measured is consistent with the change in the contents of sericin and fibroin in silks.

The variation of the thermo-mechanical properties of the cocoon along the thickness direction is clearly shown in Fig. 6. Both the storage modulus and the loss modulus increase from the outside to the inside. E' and E'' values of the innermost (the fourth) layer are significantly higher than those of the outermost (the first) layer. It can be seen that normal compact cocoons have a good damping property, which is closely related with their microstructure. Through the historical evolution of millions of years, therefore, *B. mori* silk cocoons have formed an optimum

(c)

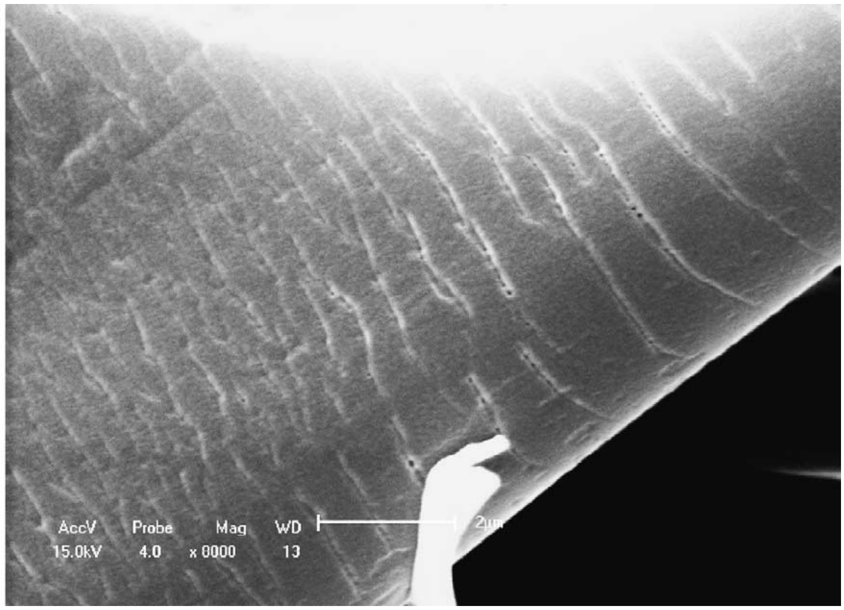

Fig. 7 (*continued*)

microstructure which creates not only the high elastic modulus and strength but also the excellent thermo-mechanical properties.

Three SEM images, which were taken after the DMTA tension test with temperature increasing from 35 to 320 °C, are given in Fig. 7 to illustrate some fracture features of the cocoons and the silks. One can clearly see the structure of the silks as consisting of two bonded threads. Each thread is composed of two fibroin fibers with diameters in the range of 7–14 μm and a coating layer of sericin with thickness in the range of 2–4 μm. Some significant characteristics and physical mechanisms of fracture of silks can be observed. First, it is observed that the critical breaking strain and energy of sericin are significantly lower than those of the fibroin fibers. The critical fracture strain and fracture energy rely strongly on the molecular and crystal structures of the considered silks. Unbinding of the two originally bonded strands of a silk can easily occur, as shown in Fig. 7(a). Second, delaminations between the fibroin core and the sericin coating often happen under tension, followed by the pullout of the fiber from the sericin layer, as shown in Fig. 7(b). This indicates that the adhesive strength between the fibroin and sericin in the silks is relatively weak. Third, many crazes have been observed on the surfaces of silks, as clearly shown in Fig. 7(c) [29,30]. This is one of the typical damage mechanisms for polymer materials [31–33]. Furthermore, it is also observed that the fracture of silks in a cocoon subjected to tension is generally of a tension–shearing mixed mode. This can be easily understood since most oriented fibers are subject to both axial tension and bending. The rough fracture surface in Fig. 7(b) results from the tension–bending mixed loading as well as the special microstructures of the silks.

4. Conclusions

A series of experiments have been performed to study the mechanical properties (elastic modulus, strength, fracture and thermo-mechanical properties) of *B. mori* silk cocoons. Silkworm caterpillars can use a limited amount of fibroin and sericin to produce cocoons to protect the moth pupas against possible impacts from the outside. Our experiments show that both the static and the dynamic properties of cocoons are superior. These properties are attributed mainly to the high strength of silks as well as to the porous and layered microstructures, comprised of a long silk bonded together by the sericin on the silk surface. On the other hand, all of the elastic modulus, strength and thermo-mechanical parameters of a cocoon vary along its thickness direction in an appropriate manner, yielding a further enhancement of its ability to resist possible attacks from the outside. In addition, some main features of the fracture process and the associated physical mechanisms of silks and cocoons have been revealed.

Our experiments indicate that silkworm larvae are worthy of praise for their ability to construct protective cocoons with an optimum microstructure and superior mechanical properties. This study is a primary effort to understand the mechanical behaviors and their dependence on the microstructures of cocoons. The obtained results might be helpful to guide biomimetic designs of novel safe-guarding materials from both the viewpoints of microstructures and spatial functional gradients.

Acknowledgements

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