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# Natural and highly protective composite structures – Wild silkworm cocoons

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ABSTRACT

Wild silkworm cocoons are thin and lightweight composite structures that provide silkworms with excellent protection against extreme temperature and other harsh weather conditions (e.g. UV, wind, rain). Understanding such natural composite structures will provide bio-inspiration for developing highly protective and light-weight fibrous materials and structures. This paper highlights our recent research on the mechanical and thermal properties, moisture transfer behaviour, and UV resistance of wild silkworm cocoons, in comparison with the domestic *Bombyx mori* silkworm cocoon. Wild silkworm cocoons such as *Antheraea pernyi* exhibit exceptionally high toughness, excellent thermal buffer, directional moisture transfer and strong UV resistance, all of which contribute to the high-level protection of the silkworm pupa in harsh outdoor environments.

## 1. Introduction

The silkworm cocoon is a multilayer composite structure formed by continuous twin silk filaments bonded by sericin [1]. Depending on the silkworm species, the cocoons vary in shape, colour, density, volume and fibrous structure [2]. In comparison with domesticated silkworm *Bombyx mori* (*B. mori*), wild silkworms require much greater protection from environmental, biotic and physical hazards [3]. The process of silk spinning and cocoon building has evolved over millions of years through natural selection [4]. As fine products of these fully developed processes, wild silkworm cocoons have a quite unique multi-layer and multi-component structure, which plays important roles in providing the protective function during the immobile phase of life cycle when the silkworm enters diapause and metamorphosis.

Silk fibres have outstanding mechanical properties. In particular, the toughness of silkworm fibres can be superior to some of the best synthetic high-performance fibres available today, including Kevlar [5]. While the outstanding fibre tensile properties are important for load bearing applications, they do not explain how silk cocoons protect wild silkworms from extreme weather conditions. In this study, we systematically examined the mechanical [3,6], thermal [2,7,8], moisture transfer [9] and UV resistance properties [10] of both domestic and wild silkworm cocoons. The comparison highlighted the unique highly protective functions of the *Antheraea pernyi* (*A. pernyi*) cocoon. Understanding the relations between structure, property and function of this important biological material will provide a conceptual platform to design and develop new lightweight protective materials.

## 2. Material and methods

### 2.1. Materials

*Bombyx mori* (*B. mori*) cocoons were purchased from silk rearing houses in Northeast India; *A. pernyi* cocoons were collected from Northeast China and *Antheraea assamensis* (*A. assamensis*), *Samia cynthia* (*S. cynthia*) and *Antheraea mylitta* (*A. mylitta*) cocoons were collected from Central India. They were received as stifled cocoons, commonly used prior to reeling silk filament for textile applications.

### 2.2. Methods

#### 2.2.1. Peel resistance of cocoon wall

The 180 degree peel tests, modified from the ASTM standard test D 1876-08 for peel resistance of adhesives, were used for examining the peel resistance of cocoon walls. A loading rate of 2 mm/min was applied to delaminate cocoon samples with the dimension of 20 mm×5 mm. Cocoon wall samples were chosen with the 20 mm edge perpendicular to the equator of the cocoon. The cocoon wall samples were peeled artificially for a length of 5 mm before they were pulled apart by the tester. Three specimens for each type of cocoons were peeled into multiple layers. The peeled layers were numbered according to the sequence from the outer to inner layers (e.g. layer 1 is the

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outermost layer). The work of fracture (WOF) was obtained by the work under the load vs. extension curves divided by the delamination area. The morphologies of the cocoons and the fracture surfaces were investigated by a scanning electron microscope (SEM) (Supra 55VP).

### 2.2.2. Needle penetration resistance

Needle penetration tests were performed on a 5967 Materials Testing System (Instron Corporation, USA) equipped with a 100 N load cell. A lab-designed test set-up was used. It consisted of a base holding the test specimen in position and a puncture probe attached with a needle for penetrating the specimen. A tension force of 2.3 N was applied to the specimen by a spring between the two mounting blocks. Three-facet 21 G hypodermic needles (Terumo Corporation, USA) with a diameter of 0.8 mm and tip angle of 19° were used for all the needle penetration tests. A loading rate of 10 mm/min was used to test samples with the dimension of 25 mm×8 mm. Cocoon wall samples were chosen with the 25 mm edge perpendicular to the equator of the cocoon. A new needle was used for each test. The mechanical property data was obtained from five test replicates.

### 2.2.3. Relative humidity measurement

The relative humidity measurements were conducted in a temperature and humidity regulated chamber (ESPEC, Model 306-421). The cocoon wall was cut into round pieces and attached to one side of a cylindrical plastic bottle. The other side of the bottle was connected to a cap, in which a hole was drilled to lead the humidity sensor into the bottle. The cocoon wall samples were obtained from the middle parts of the cocoons and kept flat when connecting to the bottles. A 2D computational fluid dynamics (CFD) model was built to simulate the process of moisture transfer through the *A. pernyi* cocoon wall. The geometry of the *A. pernyi* cocoon wall in the model was constructed based on the cross section of the natural *A. pernyi* cocoon.

## 3. Results and discussion

The morphology of cocoon from the Chinese tussah silkworm *A. pernyi* is shown in Fig. 1. By comparison with the domesticated *B. mori* cocoon, the *A. pernyi* cocoon has wider flat silk fibres [11] with cubic crystals deposited on the outer surface of the outer layer silk fibres [12]. During the interlaminar peel tests, the peeling loads were less than 1 N for the *B. mori* cocoon and the load values were comparable for three peeled layers. For *A. pernyi* cocoons, the peeling curves became more fluctuated with much higher loads (the maximum load values reached 4–5 N); the outer layers were more difficult to separate. These results indicate that delamination resistance of different *B. mori* layers is similar from outer to inner cocoon surfaces; however, the delamination resistance of *A. pernyi* cocoon layers is stronger in the outer layers. It is likely that the wild silkworms have designed a tougher outer surface to minimise damage to the cocoons in the wild. The average peeling load was 0.35 N for the *B. mori* cocoon (Table 1), but was 1.2 N and 2.5 N for the *A. assamensis* and *A. pernyi* cocoons, respectively. During peeling, the wild cocoons experienced higher peak loads than the domestic one, which transfers to a maximum work-of-fracture (WOF) of about 320 J/m$^2$ for the *A. assamensis* outer layer and 980 J/m$^2$ for the *A. pernyi* outer layer, almost 3 times and 10 times of the *B. mori* cocoon. The semi-domestic *S. cynthia* cocoon had WOF of 140 J/m$^2$ which was a seventh of the *A. pernyi* values. The cubic crystals deposited on the outer surface/layers were not shown to improve interlaminar fracture toughness, but contributed to their extremely high hardness. In contrast to the *B. mori* inner layers which had a hardness value of less than 25 MPa, the hardness of the *A. pernyi* inner layer was 125 MPa, and that of the calcium oxalate crystals was around 2 GPa. The fracture surfaces of different cocoon types from peeling tests revealed slight fibre damage at the intersections where *B. mori* silk fibres stack on top of each other. However, the fracture surfaces of *A. pernyi* cocoons showed more severe fibre splitting, indicating the stronger interlaminar bonding and fibre/matrix adhesion in these tough cocoons [6].

The needle puncture tests were conducted using a self-made experimental rig. Against the 21 G hypodermic needle, the *A. pernyi* cocoon shell showed the highest needle penetration resistance, with a maximum needle penetration load of 11.8 N, followed by the aramid fabric of 7.1 N and the much lower loads between 2 to 5 N for the *B. mori* and *S. cynthia*. The *A. pernyi* and aramid fabric specimens had smaller displacements than the *B. mori* and *S. cynthia* ones at the maximum load (Fig. 2). Three main distinctive load peaks (1, 2 and 3) were observed for each sample during penetration by the three-facet needle. Peak 1 coincided with the needle tip penetration, exposing the tip to the underside of the sample [13], peak 2 coincided with the end of the cutting induced by the upper part of the bevelled edge, reaching the underside of the sample; peak 3 represented the ejection of the bevel heel from the cut hole. After that, the needle slid easily into the hole, with a decrease in the applied force. The damages to different specimens from needle penetration were observed by SEM. In contrast to the cleanly and sharply-cut fibres from other specimens with low resistance, the *A. pernyi* showed apparent fibre kinking near the broken ends (at the needle insertion side) and large amount of fibre debris that was brought outwards following the needle perforation (Fig. 2c and Fig. 2d), indicating significant cutting involved during the puncture process.

The peel resistance and the needle penetration resistance are also closely related to the fibrous structure of the cocoon walls. As seen in Fig. 3, the cocoon fibre assembly is shown in the cross section of the cocoon walls. In contrast to the *B. mori* and the *S. cynthia*, the silk fibres are more densely packed in the *A. assamensis* and the *A. pernyi* cocoons, which contribute to the higher delamination fracture toughness and penetration resistance from these cocoon walls.

A proper relative humidity (RH) level inside of the cocoon plays an important role in the process of metamorphosis of silkworm. For the *A. pernyi* cocoon wall, the relative humidity gradient was higher in the direction from inner to outer surface of the cocoon wall than that in the opposite direction, showing directional moisture resistance [9]. Therefore the moisture resistance in the direction from outer to inner surface of the cocoon wall was higher than that in the opposite

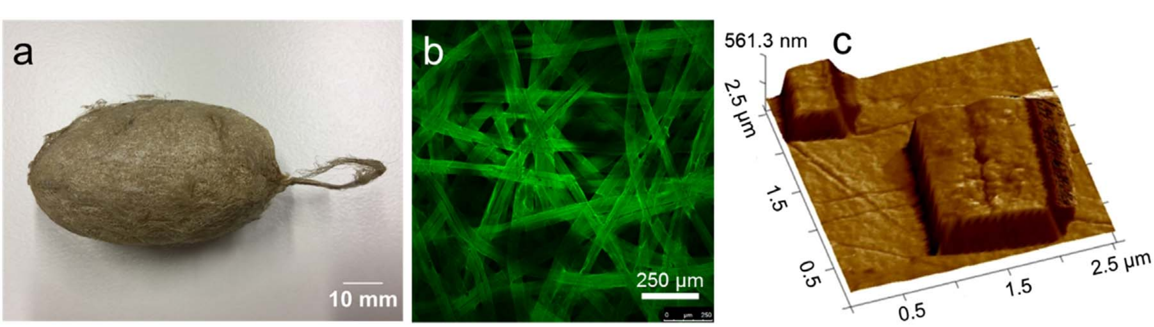


**Fig. 1.** The *A. pernyi* cocoon. a) photo of the cocoon; b) confocal image of the cocoon wall layer; c) AFM image of the calcium oxalate crystals deposited on the surface of the outer layer.