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Interactions between fibroin and sericin proteins from *Antheraea pernyi* and *Bombyx mori* silk fibers

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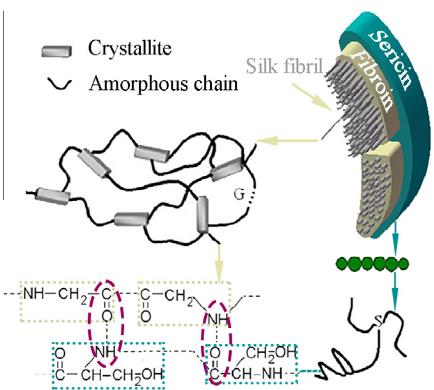
GRAPHICAL ABSTRACT



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ABSTRACT

Silkworm silk fibers are core-shell composites of fibroin and sericin proteins. Studying the interactions between fibroin and sericin is essential for understanding the properties of these composites. It is observed that compared to the domestic silk cocoon *Bombyx mori* (*B. mori*), the adhesion between fibroin and sericin from the wild silk cocoon, *Antheraea pernyi* (*A. pernyi*), is significantly stronger with a higher degree of heterogeneity. The adsorption of *A. pernyi* sericin on its fibroin is almost twice the value for *B. mori* sericin on fibroin, both showing a monolayer Langmuir adsorption. ^{1}H NMR and FTIR studies demonstrate on a molecular level the stronger interactions and the more intensive complex formation between *A. pernyi* fibroin and sericin, facilitated by the hydrogen bonding between glycine and serine. The findings of this study may help the design of composites with superior interfacial adhesion between different components.

1. Introduction

Composites have applications in many fields such as aerospace, construction, defense and land transportation [1]. The interactions between the different components affect the mechanical properties of such a material. Inspired by nature, many types of

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composite materials with super mechanical properties and functions have been designed. For example, PEE/PPy composite films inspired by the network structure of animal dermis [2], artificial composite with high resilience inspired by nacre [3], superhydrophobic surface inspired by lotus leaf [4], and alumina platelets inspired by seashells [5], have been developed for different applications.

A silkworm silk fiber is a typical natural (core-shell) composite. It consists of two types of proteins, namely silk fibroin and sericin. Silk fibroin is extruded from the posterior silk glands and forms the two silk core monofilaments. Sericin, which is hydrophilic and synthesized in the middle silk gland, glues and coats the two fibroin monofilaments. Silkworm silk has significant applications in textile and biomedical fields due to their excellent mechanical properties and excellent biocompatibility. Apart from domestic silkworm silk, wild silkworm silks, especially that of the *Antheraea pernyi*, have attracted special research attention. Attributable to its specific amino acid sequences, *A. pernyi* silk has a lower crystallinity (β sheets) and hence a lower strength, but superior elasticity and toughness, compared with its domestic counterpart, *Bombyx mori* [6,7]. The special fiber structure (e.g. high porosity) of *A. pernyi* contributes to its excellent thermal insulation property [8,9]. In addition, compared to *B. mori* silk, sericin is harder to remove from the *A. pernyi* silk [10–12]. Sericin can be easily removed from *B. mori* silk by alkaline (sodium carbonate) or hot water (Fig. 1a and b). However, they can only partially remove the sericin from the *A. pernyi* silk under the same conditions, *i.e.* temperature, salt concentration and treatment duration (Fig. 1c and d). These indicate that stronger interactions exist between the sericin and fibroin of this wild silk. The strong adhesion could also contribute to the excellent properties of the wild silkworm cocoons, protecting the worm from attack by predators or abrasion against twigs.

Despite the increasing interest in wild silk fibers, a fundamental understanding of the adhesion between sericin and fibroin of the wild silk has not been achieved. The knowledge could inspire the design of composite materials with excellent interfacial adhesion between the different components and superior properties. In this work, the adhesion and molecular interactions between fibroin and sericin of the *A. pernyi* silk are investigated with various techniques. Inverse gas chromatography (IGC) is used to examine both specific and non-specific adhesion, quartz crystal microbalance with dissipation (QCM-D) is used to characterize the adsorption dynamics of sericin on fibroin. Nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy are used to study the interactions between sericin and fibroin on a molecular level. The adhesion and interactions between fibroin and sericin from domestic silk *B. mori* are also studied to get a better understanding of the superior interfacial integrity of wild silk proteins. It is demonstrated that the stronger adhesion and interactions between proteins from the wild silk are due to more specific interactions between their glycine and serine residues. The rougher surface of *A. pernyi* fibroin fiber also contributes to the stronger adhesion.

2. Materials and methods

2.1. Materials

A. pernyi silkworm cocoons were collected from North China and *B. mori* cocoons were purchased from the silk rearing house in China.

Sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), calcium chloride ($CaCl_2$), ethyl alcohol (EtOH), lithium thiocyanate (LiSCN) and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich and were of analytical grade with a purity of at least 98%. Dialysis tubing cellulose membrane (12 kDa) and snakeskin pleated dialysis tubing (3.5 kDa) were purchased from Sigma-Aldrich and Thermo Fischer Scientific, respectively. Deionised (DI) water was used throughout the study. Deuteroxide (D_2O, 99%, Sigma-Aldrich) was used for NMR tests.

2.2. Methods

2.2.1. Preparation of sericin proteins

A base degumming method was used to obtain sericin from both the *A. pernyi* and *B. mori* silk. Briefly, a mixed solution of 1% base (sodium carbonate plus sodium bicarbonate in equal weight

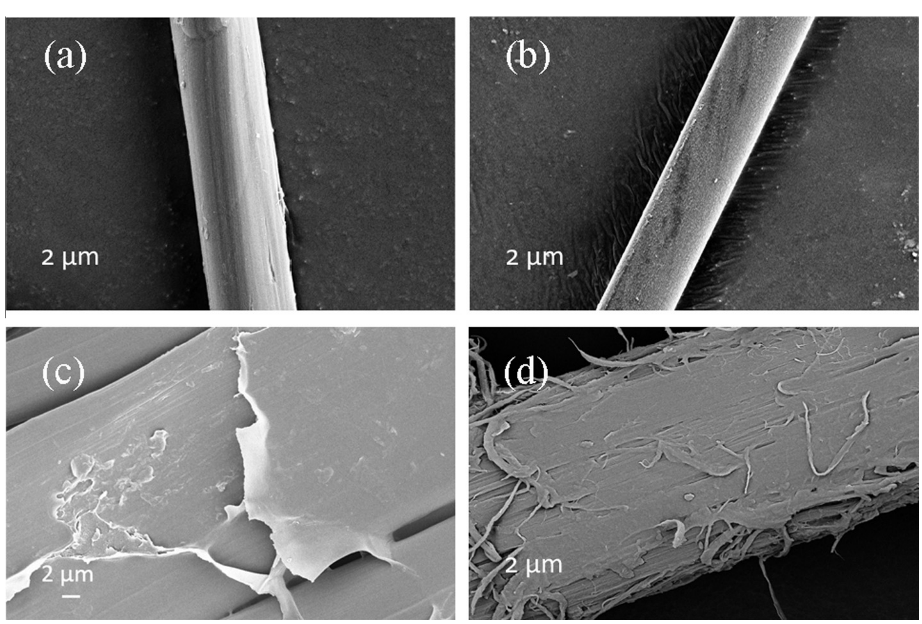

Fig. 1. *B. mori* (a and b) and *A. pernyi* (c and d) silk fibers degummed with a sodium carbonate solution (a and c) and water (b and d) at 98 °C with a fiber (g) to solvent volume (mL) ratio of 1:40.