Materials Science and Engineering C 34 (2014) 417–421

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Directly obtaining high strength silk fiber from silkworm by feeding carbon nanotubes

Jun-Ting Wang, Lu-Lu Li, Meng-Yuan Zhang, Si-Lu Liu, Lin-Hai Jiang, Qing Shen *

State Key Laboratory for Modification of Chemical Fiber and Polymers, and Polymer Department of Donghua University, 2999 N. Renmin Rd. Songjiang, 201620 Shanghai, China

ARTICLE INFO

Article history:
Received 12 October 2012
Received in revised form 21 September 2013
Accepted 28 September 2013
Available online 8 October 2013

Keywords:
Silk fiber
Silkworm
Carbon nanotubes
Feeding
Strength

ABSTRACT

By feeding silkworm with the carbon nanotube, CNT, we directly obtained high strength silk fiber, SF, from silkworm. The CNT-based SF, SF/CNT, has a stress at 1.69 GPa and a strain at about 24% both higher than those of the SF and are capable to compare with the super SF and even the spider fiber. Morphology comparison showed that the presence of CNT in SF caused the cross-section changed from triangle to ellipse. X-ray diffraction and infrared analysis indicated that the embedded CNT in SF caused an increase in silk-I structure. Specifically the amide-II structure reduced by about 5% and the amide-III structure increased by about 10%. Thermogravimetric analyses indicated that the presence of CNT in SF enhanced the thermal stability. Additionally, the presence of CNT in SF also enhanced the electrical property.

1. Introduction

Bombyx mori silk fiber, SF, is a semicrystalline biopolymer with 80–85% of glycine, alanine and serine. SF has for a long time been applied in textile, biotechnological and biomedical fields due to its high strength, rupture elongation, environment stability and biocompatible properties [1–4]. In order to obtain SF with enhanced mechanical or functional properties, a lot of work has been tried as can be seen elsewhere which including the chemical modifications [4,5], adjustment of the harvesting parameters [6] and reconstruction of SF via the artificial spinning by adding some nano- or functional materials to mix with silk protein [4–20]. The use of carbon nanotube, CNT, to reinforce SF has been tried in an artificial spinning process and the presented regenerated SF, RSF, has been found to have enhanced mechanical and electrical properties [4,17–29].

In addition, it is also noted that Shao and Vollrath have reported a special case to obtain reinforced pristine SF [6] by fixing the head of silkworm to forbid its random motion during the fiber spinning process and meanwhile to increase the spinning speed by using an extra winder. According to these researchers' reported values, the strength enhancement is limited for SF because the stress increase is accompanied with the strain loss or on the contrary [6].

In this work we reported a simple method to obtain in vivo reinforced SF directly from silkworm. Experimentally, we reared twelve silkworms at the laboratory, and fed them with two kinds of mulberry leaves, MLs. One is the normal ML as obtained from the tree and another is the ML pretreated by spreading lignosulfonate, LGS, to modify CNT on the ML surface to form ML/CNT. Our results showed that this method can lead to SF with enhanced mechanical and electrical properties and these data are comparable with literature reported cases on strength enhanced SFs [4–20].

2. Experimental

2.1. Materials

In this work, twelve *B. mori* larval silkworms were reared on an artificial diet at our laboratory. The normal MLs were obtained from the local market and washed by water then kept in a wet condition to keep its moisture at about 10%.

The MLs/CNTs were prepared as below described.

2.2. Treatment of mulberry leaves by spreading of carbon nanotubes

In this case, the used CNTs are multiwalls type with the purity above 90% purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. As known, these CNTs were formed by the chemical vapor deposition and their lengths are ranged from several hundred nanometers to several micrometers with an average outer diameter about 10–30 nm [31].

The used LGS is a calcium-based sample with an average molecular weight of 100,000 provided by Jiangmen Sugar Cane Chemical Factory, Guangdong of China. According to the producer, this LGS is composed of phenylpropane segments and sulfuric acid groups, and its lignin component is more than 55%, its deoxidized sugar is less than 12%, its

* Corresponding author. Tel./fax: +86 21 62822096.
E-mail address: sqing@dhu.edu.cn (Q. Shen).

0928-4931/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.msec.2013.09.041

water-insoluble components are smaller than 1.5%, and its moisture is at about 9%. The pH of this LGS is known to be in the range of 5–6. This LGS was directly used as received without further purification as we recently reported [31].

The modification of CNTs by LGS was started by mixing 0.5 g CNTs with 5 g LGS in an agate mortar for 3 h by hand. During this process, a small amount of water was added to avoid agglomeration. The obtained brownish slurry was added to the 200 mL buffer and was subsequently sonicated using an ultrasonic tip to stimulate the micelle formation. After that, the mixed solution was again sonicated for about 30 min and centrifuged at 15,000 rpm to remove the residual solid mass. The obtained LGS treated CNTs were washed three times by 300 mL distilled water for each one to remove the excess LGS. The prepared LGS treated CNTs were finally oven dried with measured moisture at about 10% then applied to spread on the ML surface to feed silkworms.

The use of LGS to modify CNT is based on two reasons, the first is that the LGS is also a natural biomaterial obtained from plant closing the MLs that may fit the worms, and the second is that the LGS is usually associated with some metal ions thus considered to help CNT mix well with silk protein [4,30].

2.3. Silk fiber preparation

The obtained cocoons were immersed in warm water (about 80–90 °C) with a pH of about 9–10 for about 1–3 h then the SF was hand winded on a glass bottle surface. The collected SF was prepared in a length of about 2–3 m then oven dried at 90 °C for 24 h to keep the moisture constant in a range of 3–5%.

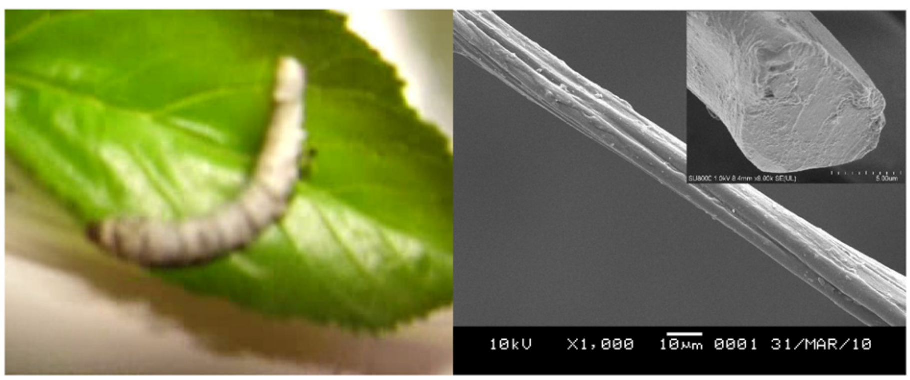
2.4. Measurement and characterization

2.4.1. Scanning electron microscopy

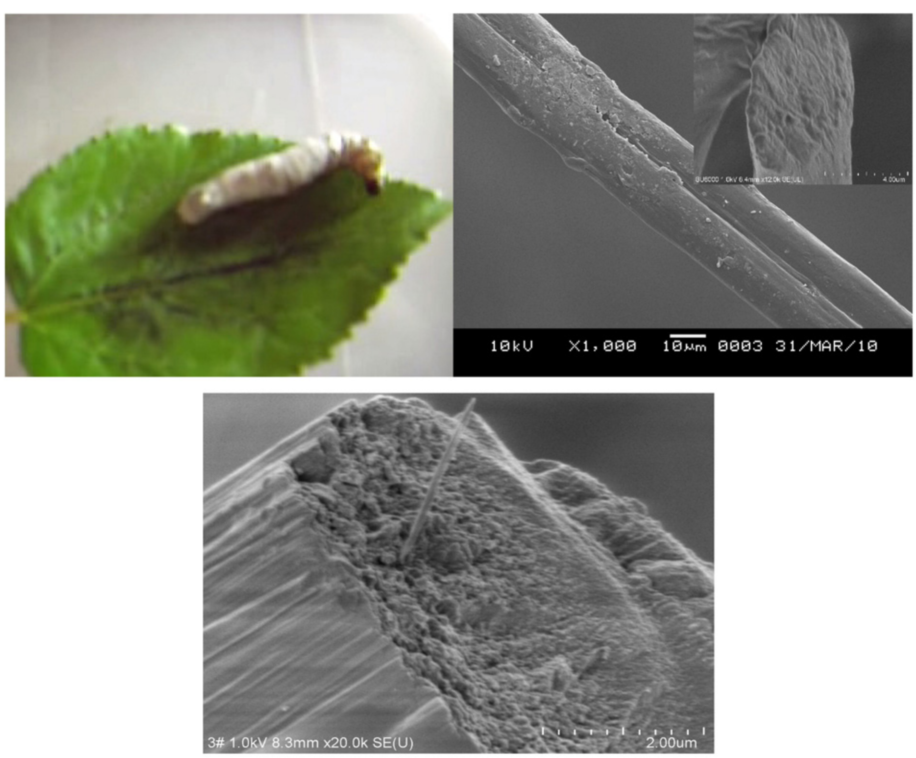
The morphology of SF was analyzed by a scanning electron microscope, SEM, (JSM-5600LV) with an accelerating voltage of about 10 kV and a magnification of 500–160,000× [31–35].

2.4.2. Thermogravimetric analyses

Thermogravimetric analyses (TGA) were conducted on a NETZSCH TG 209 at a heating rate of 10 °C/min and a nitrogen flow rate of 20 mL/min.



(a)



(b)

Fig. 1. A comparison of the morphology of silk fiber, SF, (top) and CNT-embedded silk fiber, SF/CNT (bottom).