

Spider Silk/Polyaniline Composite Wire

Hiromasa Goto *, Ryosuke Kikuchi and Aohan Wang

Division of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan; 1210990@u.tsukuba.ac.jp (R.K.); s-awang@ims.tsukuba.ac.jp (A.W.)

* Correspondence: gotoh@ims.tsukuba.ac.jp; Tel.: +81-298-85-5128; Fax: +81-298-53-4490

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Abstract: Polymerization of aniline in the presence of spider silk produces a natural fiber-based conducting polymer wire. We observed the fiber structure with polarizing optical microscopy and scanning electron microscopy. This spider-silk/PANI, a biosynthetic composite, could be the basis for organic high-performance conducting wire.

Keywords: spider; polyaniline; polymerization; SEM; polymer wire

1. Introduction

Spider silk has been studied recently because of its tremendous strength and flexibility [1]. Biotechnology now opens possibilities for the application of spider silk [2–7]. We describe a new avenue for the application of spider silk in textile science and industry. Recently, spider silk/carbon nanotube composites have been prepared, and their mechanical and electrical properties characterized. For example, textile transistors were fabricated with a silk/carbon nanotube composite [8]. Combinations of organic conductors and spider silk might realize organic molecular wires with electrical conduction, light emission, and photovoltaic functions.

Polyaniline (PANI) is one of the most promising electrically conducting polymers because of its moderate electrical conduction, anticorrosive function, and convenient water-based synthetic process. The combination of natural fibers and conducting polymers can produce biocompatible materials [9]. A new achievement reported here is the preparation of a biosynthetic composite consisting of spider silk as a high performance natural silk with PANI as a conducting polymer.

2. Experimental Section

2.1. Spider Silk

Spider silk was sampled directly from a single spider web in June 2015 (University of Tsukuba). The spider species was not identified. The sample involves several kinds of silk forms because spiders produce several different kinds of silk in the web. Figure 1 shows an image of a spider (*Nephila clavata*) and web. Figure 2 shows a polarizing optical microscopy (POM) image of spider silk wire which exhibited birefringence. Figure 3 displays scanning electron microscopy (SEM) images of thin lines of the spider silk.



Figure 1. A spider and web.

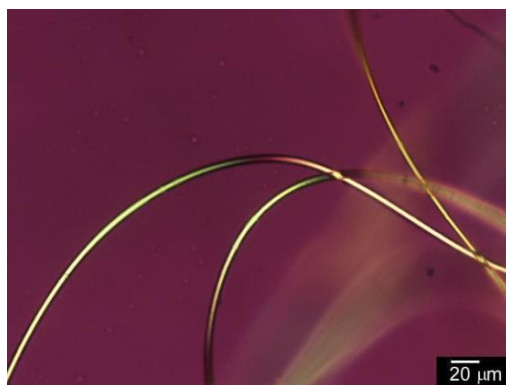


Figure 2. Polarizing optical microscopy image of spider silk.

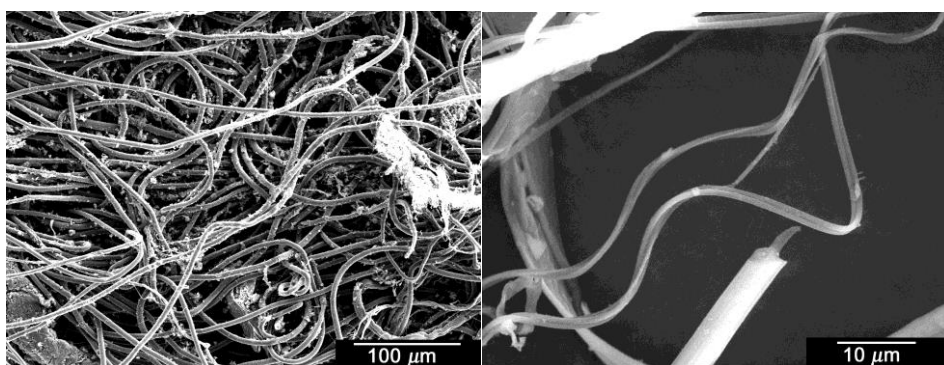
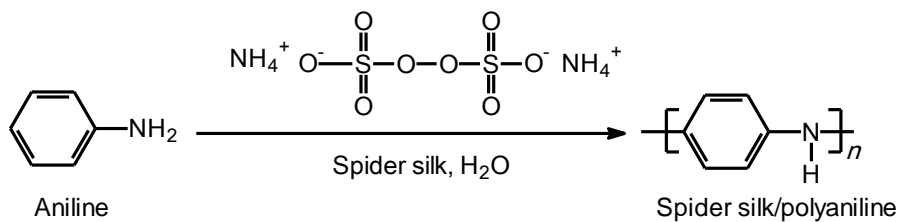


Figure 3. Scanning electron microscopy images of spider silk.

2.2. Polymerization of Aniline in the Presence of Spider Silk

The spider silk was immersed in distilled water. Aniline as a monomer and sulfuric acid were added to the solution. After the mixture was stirred for 30 min, ammonium per sulfate (APS) was added followed by cooling to 0 °C (Scheme 1). After 24 h, the solution was filtered, and the crude product washed with a large volume of water, followed by filtration. Subsequently, the resultant cake was added to a large volume of methanol. Filtration followed by drying under low pressure afforded spider silk/polyaniline. PANI was coated on the surface of the spider silk, Figure 4a.



Scheme 1. Polymerization of aniline in the presence of spider silk.

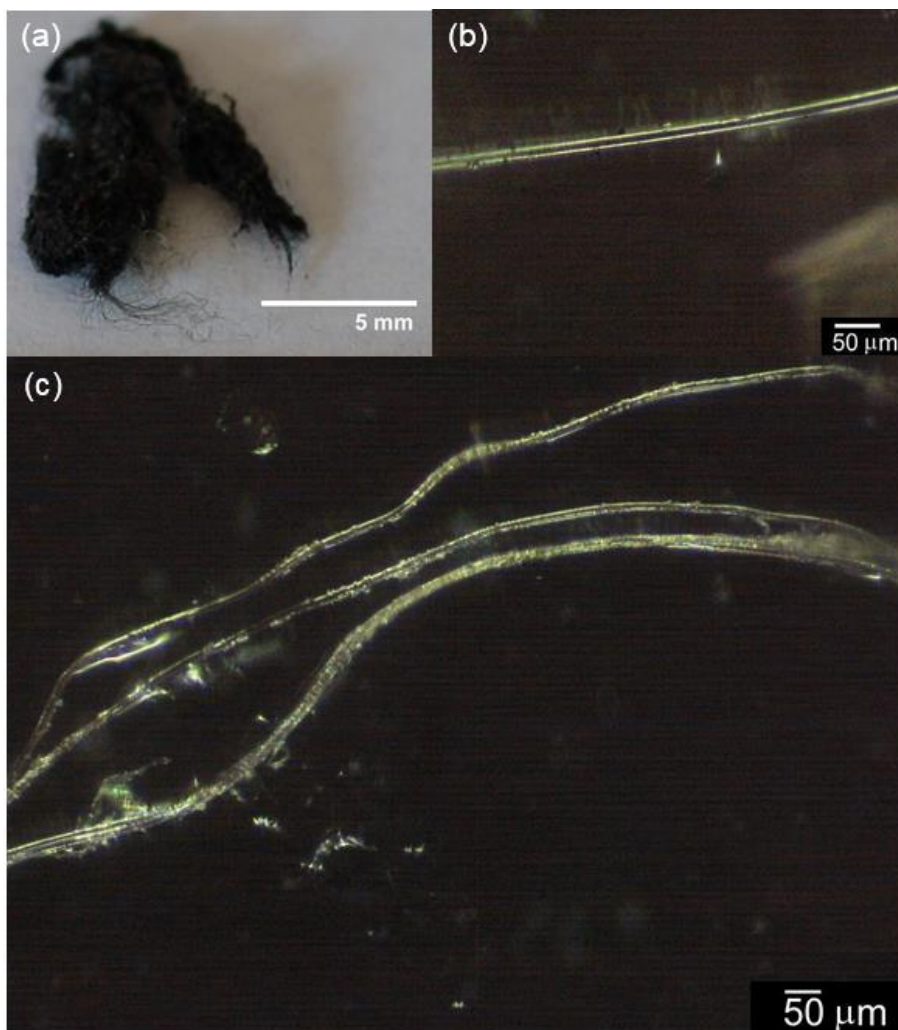


Figure 4. (a) Photograph of silk/polyaniline; (b,c) Optical microscopy images of silk/polyaniline at different magnifications.

3. Results and Discussion

3.1. Surface Observation

Figure 4b,c display optical microscopy images of the spider silk/polyaniline. An emerald green color of the fiber indicates that the spider silk surface is covered with PANI. Figure 5a,b show SEM images of the resultant spider silk/polyaniline, indicating that polyaniline is coated on the silk surface. Polymerization in the presence of surfactant (e.g., dodecyl benzene sulfonate, DBS) would produce a smooth surface. Figure 6 is a plausible structure of the spider silk/polyaniline composite.

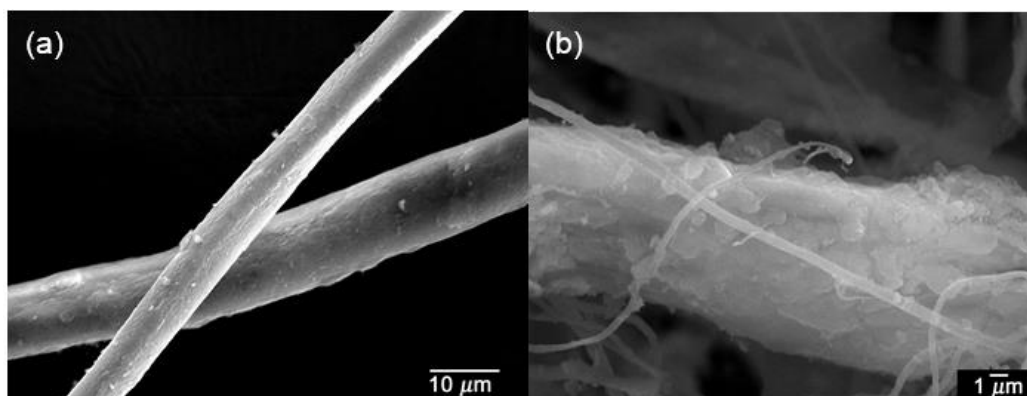


Figure 5. Scanning electron microscopy images of spider silk/polyaniline. (a) 1600 \times ; (b) 4300 \times .

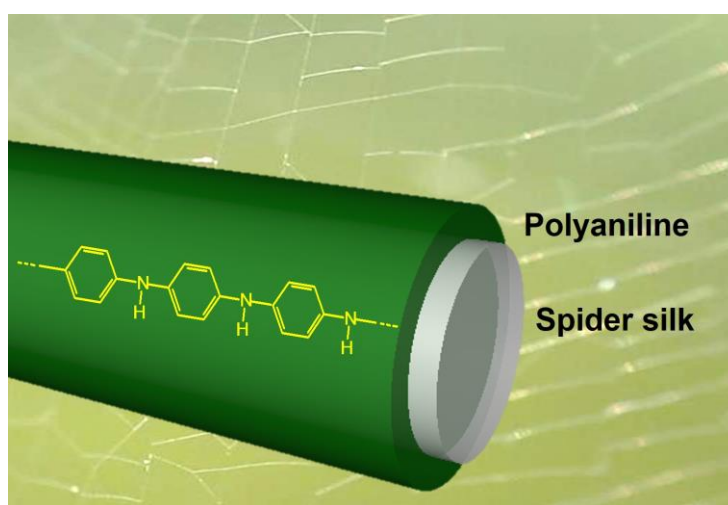


Figure 6. Plausible structure of spider silk/polyaniline.

In the polymerization process, the surface of the spider silk can play the role of a reaction field, absorbing aniline monomer by capillary effect in the water medium before polymerization. Thus, a high concentration of monomer aniline is distributed on the surface of the spider silk wire. Then, polymerization is initiated with addition of APS. After the polymerization, the PANI layer is deposited on the spider silk surface to form a biocomposite—an artificial biopolymer composite polymer composite.

3.2. Infrared Absorption

Figure 7a shows infrared absorption spectra of the spider silk/polyaniline using the KBr method. An intense absorption band at 3304 cm^{-1} is assignable to ν_{OH} of the silk. An absorption band at 2950 cm^{-1} is due to stretching vibrations of CH and CH_2 of the silk. An absorption band due to the quinoid structure (Figure 8) of the polyaniline is observed at 1660 cm^{-1} . An absorption band from the benzenoid structure in the polyaniline is seen at 1532 cm^{-1} . The IR with the KBr method result confirms that the resultant composite consists of silk and polyaniline. The absorption band at 2950 cm^{-1} is due to the CH_2 and CH stretching of silk. Amide I (C=O stretch, $1700\text{--}1600\text{ cm}^{-1}$), amide II (N–H bending and C–N stretching, $\sim 1550\text{ cm}^{-1}$), and amide III (N–H bending and C–N stretch, $1200\text{--}1250\text{ cm}^{-1}$) [10], due to protein structure of spider silk, are overlapped with absorptions of PANI.

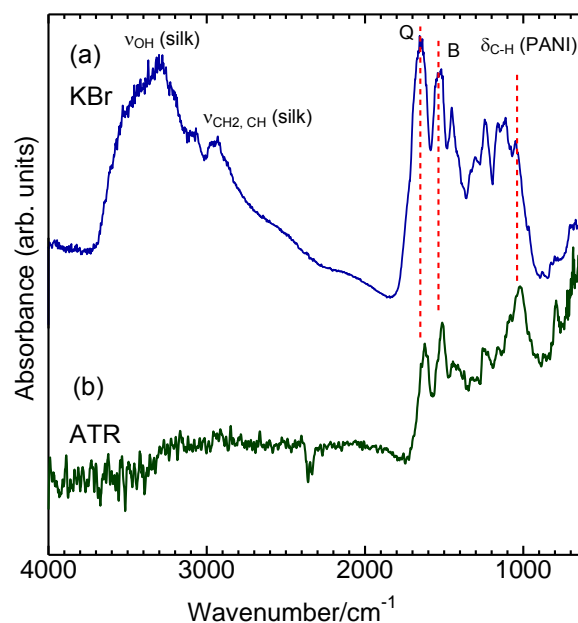


Figure 7. Infrared spectrum of the spider silk/polyaniline. (**Top**): KBr method; (**Bottom**): attenuated total reflection method. Q = quinoid, B = benzenoid.

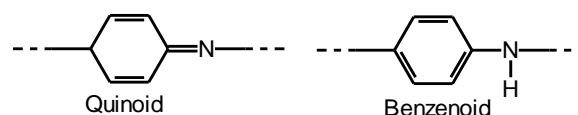


Figure 8. (**Left**): Quinoid (Q); (**Right**): Benzenoid (B).

Further, attenuated total reflection (ATR) measurement indicates that the surface is covered with a PANI layer, because the absorption bands derived from proteins (νOH , νCH , and νCH_2) are not observed in the ATR, Figure 7b.

Assignment of the absorption bands for spider silk/PANI is summarized in Table 1 [11], although slight differences between the absorption bands of the composite obtained from the KBr and the ATR methods were observed. Ion exchange between KBr and the PANI dopant (H_2SO_4) and possible mechanical degradation of the fibers under the pressure of preparation of the cast disk may occur. Although such slight differences of the signal position were observed, the absorption bands of the spider silk/PANI composite could be assigned. Therefore, the IR measurement confirms that the resultant material is a PANI and silk composite.

Table 1. Assignment of the IR spectra of spider silk/PANI with KBr and ATR methods.

Assignment	KBr ^a	ATR ^b
	Wavenumber (cm^{-1})	
OH str. ^c	3304	-
CH and CH_2	2950	-
Quinoid	1660	1623
Benzenoid	1532	1515
Str. ^c of benzene ring	1451	1452
C–N str. in BBB	1241	1253
C–H ip ^d on 1,2,4-ring	1049	1028

Notes: ^a KBr method; ^b attenuated total reflection (ATR) method; ^c stretching; ^d in plane.

3.3. Electrical Properties

Figure 9 displays the current as a function of voltage for the spider silk/polyaniline. The current is proportional to applied voltage, indicating electrical conduction of the composite. Electrical conductivity of the bulk sample (not single fiber) was to be 5.7×10^{-6} S/cm.

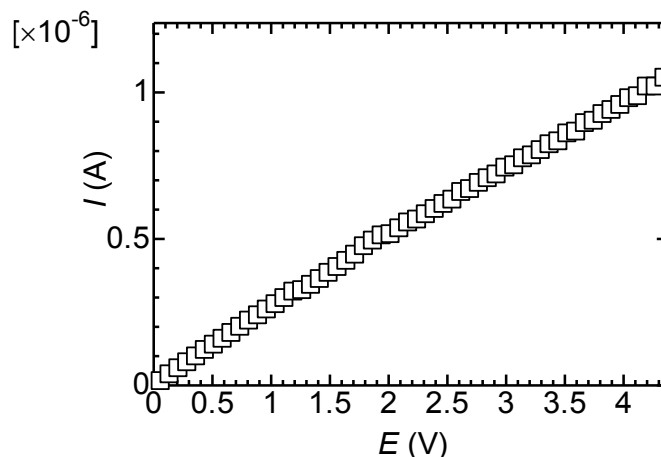


Figure 9. Current (I) vs. voltage (E) for the spider silk/polyaniline.

4. Conclusions

Polymerization of aniline in the presence of spider silk was carried out to obtain natural-product-based polymer wire. Surface structure and the IR measurements of the wire indicate the formation of a composite. Additionally, the combination of strength and conductivity of the polyaniline may lead to the production of a new organic conductive wire. The spider silk/PANI is stronger than PANI alone.

Techniques: Infrared (IR) absorption spectroscopy measurements were conducted using a J-550 (JASCO, Tokyo, Japan) with the KBr method. ATR-IR spectra of the composite were obtained using a Thermo Scientific NICOLET iS5 (Thermo Fisher Scientific, Kanagawa, Japan). SEM observations were performed with a JEOL JSM-7000F (JEOL, Tokyo, Japan). I vs. E measurement was carried out with HIOKI 3522-50 LCR HiTESTER (HIOKI, Ueda, Japan). Electrical conductivity was measured by the four-probe method using Mitsubishi Chemical Analytech LORESTA-GP MCP-T610 (Mitsubishi Chemical Analytech, Chigasaki, Japan).

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Author Contributions: Hiromasa Goto directed this research. He sampled the spider silk, carried out synthesis of the spider silk/polyaniline, and observed the composite with POM and electrical measurements. Ryosuke Kikuchi performed SEM observations and IR measurements. Aohan Wang carried out SEM observations and drew the plausible structure (Figure 6).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Osaki, S. Spider silk as mechanical lifeline. *Nature* **1996**, *384*. [[CrossRef](#)]
2. Humenik, M.; Smith, A.M.; Scheibel, T. Recombinant spider silks—Biopolymers with potential for future applications. *Polymers* **2011**, *3*, 640–661. [[CrossRef](#)]
3. Kuwana, Y.; Sezutsu, H.; Nakajima, K.; Tamada, Y.; Kojima, K. High-toughness silk produced by a transgenic silkworm expressing spider (*araneus ventricosus*) dragline silk Protein. *PLoS ONE* **2014**, *9*. [[CrossRef](#)] [[PubMed](#)]

4. Teulé, F.; Miao, Y.G.; Sohn, B.H.; Kim, Y.S.; Hull, J.J.; Fraser, M.J., Jr.; Lewis, R.V.; Jarvis, D.L. Silkworms transformed with chimeric silkworm/spider silk genes spin composite silk fibers with improved mechanical properties. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 923–928. [[CrossRef](#)] [[PubMed](#)]
5. Xia, X.-X.; Qian, Z.-G.; Ki, C.S.; Park, Y.H.; Kaplan, D.L.; Lee, S.Y. Native-sized recombinant spider silk protein produced in metabolically engineered *Escherichia coli* results in a strong fiber. *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 14059–14063. [[CrossRef](#)] [[PubMed](#)]
6. Futahashi, R.; Okamoto, S.; Kawasaki, H.; Zhong, Y.S.; Iwanaga, M.; Mita, K.; Fujiwara, H. Genome-wide identification of cuticular protein genes in the silkworm, *Bombyx mori*. *Insect. Biochem. Mol. Biol.* **2008**, *38*, 1138–1146. [[CrossRef](#)] [[PubMed](#)]
7. Fredriksson, C.; Hedhammar, M.; Feinstein, R.; Nordling, K.; Kratz, G.; Johansson, J.; Huss, F.; Rising, A. Tissue response to subcutaneously implanted recombinant spider silk: An *in vivo* study. *Materials* **2009**, *2*, 1908–1922. [[CrossRef](#)]
8. Steven, E.; Saleh, W.R.; Lebedev, V.; Acquah, S.F.A.; Laukhin, V.; Alamo, R.G.; Brooks, J.S. Carbon nanotubes on a spider silk scaffold. *Nat. Commun.* **2013**, *4*. [[CrossRef](#)] [[PubMed](#)]
9. Xia, Y.; Lu, X.; Zhu, H. Natural silk fibroin/polyaniline (core/shell) coaxial fiber: Fabrication and application for cell proliferation. *Compos. Sci. Tech.* **2013**, *77*, 37–41. [[CrossRef](#)]
10. Paquet-Mercier, F.; Lefèvre, T.; Auger, M.; P'ezolet, M. Evidence by infrared spectroscopy of the presence of two types of β -sheets in major ampullate spider silk and silkworm silk. *Soft Matter* **2013**, *9*, 208–215. [[CrossRef](#)]
11. Tang, I.; Jing, X.; Wang, B.; Wang, F. Infrared spectra of soluble polyaniline. *Synth. Met.* **1988**, *24*, 231–238. [[CrossRef](#)]



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