

Graphitization behavior of iodine-treated *Bombyx mori* silk fibroin fiber

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Received: 21 December 2008 / Accepted: 9 May 2009 / Published online: 9 June 2009
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Abstract In order to investigate the graphitization behavior of *Bombyx mori* silk fibroin (SF) fibers, structural inspection of carbonized SF fibers treated with iodine vapor was studied at different temperatures, from 800 to 1400 °C. Wide angle X-ray diffraction measurement suggested that both untreated and iodinated SF fibers exhibited amorphous structure carbonized to 1200 °C. After carbonization at 1400 °C for 12 h, a graphite-like structure was obtained. Raman spectroscopy and transmission electron microscopic observation showed that the graphite layers of SF fibers became more ordered after iodine treatment. The carbon yield obtained at higher temperature (1400 °C) after iodine treatment was higher, ca. 28 wt%, than that of untreated SF.

Introduction

Silk-based carbon is an attractive raw material for the applications in bio- and electrochemical fields, such as, wound dressing; hydrogen storing materials; hazardous substance decomposer; electric double layer capacitor; electrode of fuel cells; electro conductive ink and electro conductive paste for higher electro conductivity performance; and thermal conductive paste, thermal conductive

sheet, and various heat dissipation composite materials [1–7].

Recent researches have revealed that iodine is a good stabilizing agent for producing higher yield carbon materials [8–12]. Kajiura et al. [8] prepared the pitches by the direct reaction with iodine at a temperature near the softening point of the parent pitch and then carbonized them at 1073 K. The iodine treatment was effective at increasing the carbon yield, and it also changed optical microstructure of the carbonized substance from flow type of isotropic. Miyajima et al. [9, 10] obtained an extremely high carbon yield, over 90 wt%, of iodine treated coal tar pitch and explained the dehydrogenative polymerization as a charge transfer complex caused by iodine treatment during carbonization of pitches. Furthermore, iodine treatment process has also been performed on other polymeric precursors, such as, polyacrylonitrile [11], poly(vinyl alcohol) [12], in order to produce high performance and high functional carbon materials and resultantly some interesting features accompanied by high carbon yield were found.

Many researchers reported on the carbonization process of silk fibroin (SF) fibers [13–17]. The carbonization of silk fibers at 800 °C was investigated and non-graphitizing carbon was obtained with a carbon yield of 30% [13]. A novel nitrogen-rich carbon material, silk carbon, was prepared from SF by simple heat treatment under inert atmosphere and the activation of the silk carbons with steam and potassium hydroxide provided nitrogen-containing activated carbons (ACs) with different pore-size distribution [14]. In the application to electric double layer capacitors, the silk carbon-based ACs showed a higher capacitance and an excellent electrochemical stability in the high voltage region, compared with a typical AC prepared from phenolic resin.

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Recently, the authors have shown that iodine is an excellent stabilizing agent for producing higher yield silk-based carbon materials [15, 16]. We produced carbon fibers from SF fibers treated with iodine vapor at 100 °C for 12 h and then carbonization was carried out by heating to 800 °C in Ar atmosphere at a multi-step carbonization process (at a nearly constant decomposition rate of silk in order to inhibit the rapid thermal decomposition). Both strength and the carbon yield (yield 36 wt% in case of *Bombyx mori* SF, and 39 wt% in case of *Antheraea pernyi* SF) of the carbon fibers obtained were considerably increased after iodine treatment. The structures of the carbon fibers obtained at 800 °C from both untreated and iodinated SF were almost the same and amorphous. However, until recently, graphitization behavior of SF has not been studied yet.

The graphite fiber is a high modulus material used for many sophisticated material applications. In the beginning of graphite fiber production, regenerated cellulose fiber (rayon) was used as a starting raw material [18, 19]. Heretofore, it was replaced by polyacrylonitrile fibers owing to its special advantages, like high yield and stretchability during pyrolysis that leads to higher crystallinity and orientation. The possibility of using SF for graphite fiber production attracts our attention for its higher yield after carbonization with iodine treatment in comparison with cellulose fibers and as well as for higher order crystalline structure of silk. In this study we examined the graphitization behavior of iodinated SF fiber at a temperature between 800 and 1400 °C and elucidated the crystalline structure using Raman spectroscopy, wide angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), and elemental analysis.

Experimental

Materials

The dominant *Bombyx mori* (*B. mori*) SF was used in the experiment. In order to remove sericin from the raw silk, the degumming process was achieved by the standard Marseille soap/soda ash method [20]. This process removed almost all the sericin. The degummed SF fiber was soft and smooth with a fine sheen.

Iodine treatment

The iodine treatment of SF fiber was carried out as follows: an adequate quantity of SF fiber was enclosed with abundant iodine in a glass vessel. After sealing the glass vessel, it was placed in an oven heated at 100 °C where iodine was vaporized and kept for several periods. The color of SF

fiber turned to dark brown by the treatment. The iodine sorption content was calculated by measuring the weight change of the SF fibers before and after the iodine treatment.

We used SF fibers treated with iodine vapor at 100 °C for 12 h for experiments.

Graphitization

SF fibers were heated to different temperatures, 800, 1000, 1200, and 1400 °C in a tubular furnace under an Ar flow using a multi step carbonization process, which was defined based on the optimum thermal degradation rate of silk. The fibers were maintained at the temperature of 1400 °C for 12 h to observe the graphitization behavior of SF fibers. The detailed heating conditions were described in our previous report [15]. In brief, to determine the heating condition of SF fiber, dynamic thermogravimetric analysis (dynamic TGA) was performed using constant reaction control (CRC) mode at -0.001 wt\%/s of constant weight reduction rate from room temperature to 800 °C with a Rigaku Thermo plus II TG 8120 under an Ar atmosphere. According to the dynamic TG result, we defined a multi step heating schedule for carbonization and the untreated and iodinated specimens were heated from 25 to 800 °C in a tubular furnace under an Ar gas flow using the multi step heating condition. Then samples were graphitized to 1400 °C for 12 h.

Sample preparation

We used 10 individual lots of degummed SF fibers for the experiments. Each lot was divided into two sub portions. In each lot, one portion was observed as original specimen and another portion was treated with iodine vapor at 100 °C for 12 h. Finally, untreated and iodinated specimens of 10 individual lots were graphitized at desired temperatures and used for different experiments.

Measurements

The weight loss percentages of untreated and iodinated SF were determined by measuring the weight change of the SF fibers before and after carbonization at different temperatures.

Raman spectroscopy was measured by S. T. Japan, Inc. HoloLab-5000, equipped with a MK-II filtered probe head using Nd: Yttrium Aluminum Garnet (YAG) laser beam of 532 nm generated at 50 mW. The measurement was carried out under the conditions of resolution of 2.5 cm^{-1} with 10 s exposure 10 times.

Wide angle X-ray diffraction (WAXD) profile was obtained by a Rigaku Rotorflex RU-200B diffractometer

using Ni-filtered CuK_α radiation generated at 40 kV and 150 mA.

Transmission electron microscopic (TEM) observation was conducted at an acceleration voltage of 200 kV using JEOL JEM-2010 instrument.

The elemental analysis was performed on a Parkin-Elmer 2400 II analyzer using the normal procedure.

Results and discussion

Figure 1 shows XRD patterns of iodinated SF carbonized at different temperature from 800 to 1400 °C. From the results, it was observed that at 800 °C, one broad peak was exhibited at $2\theta = 24.3^\circ$ for both untreated and iodinated SF, which indicates an amorphous structure. This peak remained through carbonized to 1200 °C. When the specimen was carbonized at 1400 °C for 12 h, peaks at $2\theta = 26.0^\circ$ (lattice spacing, $d = 3.42 \text{ \AA}$) was developed,

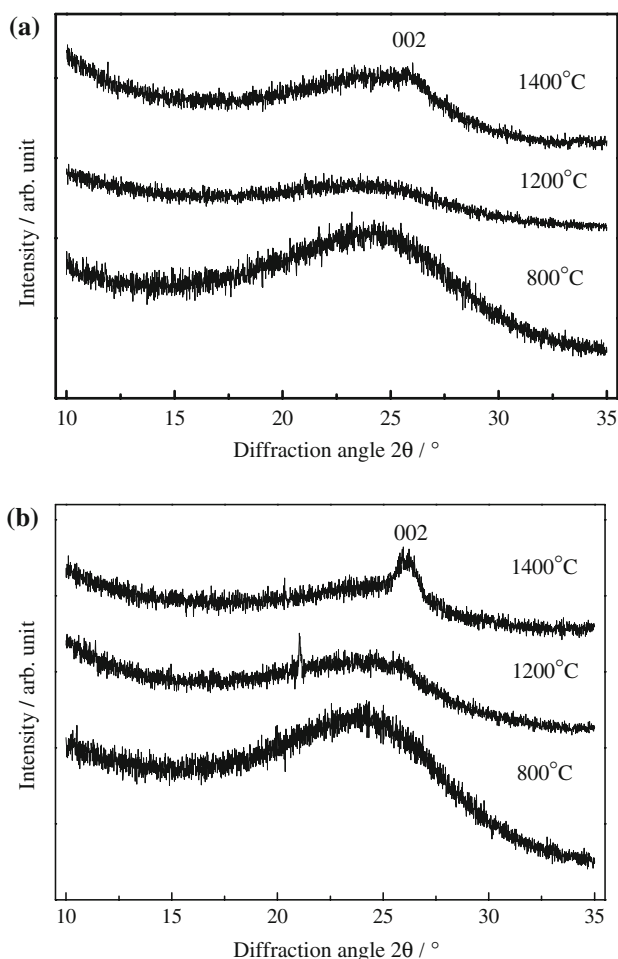


Fig. 1 Equatorial WAXD profiles of carbon fibers prepared from untreated and iodinated SF carbonized at 1400 °C for 12 h: (a) untreated specimen, (b) iodinated specimen

which corresponds to the scattering from the (002) plane of graphite [21]. Therefore, a graphite-like structure for the carbonized SF obtained at the heating temperature of 1400 °C is likely. In case of iodinated SF, the (002) peak is more visible, which suggests that iodine treatment has influenced SF molecules to build a graphite-like structure.

Raman spectroscopy has been utilized to study the deformation micromechanics of a large number of polymeric incompletely crystallized materials with cracks, internal stress, etc. [22, 23]. Generally, carbons show mainly two Raman bands, one at ca. 1580 cm^{-1} and another at ca. 1360 cm^{-1} . The former corresponds to the E_{2g} mode of graphite, known as graphite peak (G band) and is assigned to the “in-plane” displacement of the carbons strongly coupled in the hexagonal sheets. The latter, which is absent in the single crystal graphite, known as disorder peak (D band) due to discontinuity of hexagonal carbon layer planes such as finite crystallite size and also to edge planes of crystallites [22]. Consequently, a linear relation was found between the ratio of areas of the D and G band (I_D/I_G) [24, 25]. In addition to the I_D/I_G ratio, other graphitization parameters such as the peak position and the full-width at half-maximum of G band (P_G and FWHM_G) and the width of the D band (FWHM_D) were proposed [26, 27]. The width of the two bands decreased with increasing graphite order and the P_G is shifted from higher wavenumbers to the position of graphite. Figure 2 shows the Raman spectra of carbon fibers prepared from untreated and iodinated SF at 1400 °C for 12 h. Observed results are plotted with gray closed circles. Black broken and solid lines represent the deconvoluted and total curves, respectively, which were fitted by Gaussian function. Table 1 represents the peak position, the FWHM, and the intensity ratio of the two peaks, I_D/I_G obtained from the Gaussian fittings. The spectra of untreated SF showed two peaks at 1350 cm^{-1} for D band and at 1587 cm^{-1} for G band. The peaks are broad and are similar to a pattern of diamond-like carbon which possesses low crystallinity and mixture of sp^2 and sp^3 carbons. After iodine treatment, the intensity ratio of I_D/I_G and the two bands widths are decreased. Furthermore, P_G is shifted from 1587 to 1580 cm^{-1} , which is an indication that the graphite-like layers in the SF fibers became more ordered after iodine treatment.

Figure 3 shows the TEM images of carbon fibers prepared from untreated and iodinated SF at 1400 °C for 12 h. Both the carbon fibers exhibited layered structure with disordering in some part. Especially, in case of iodinated SF, it has been shown carbon layers with an average thickness of 0.38 nm, as similar as expected from the XRD pattern, developed over a scope as wide as tens of nanometers in size.

Figure 4 shows the results of elemental analysis for the carbon fibers prepared at 1400 °C for 12 h. For untreated

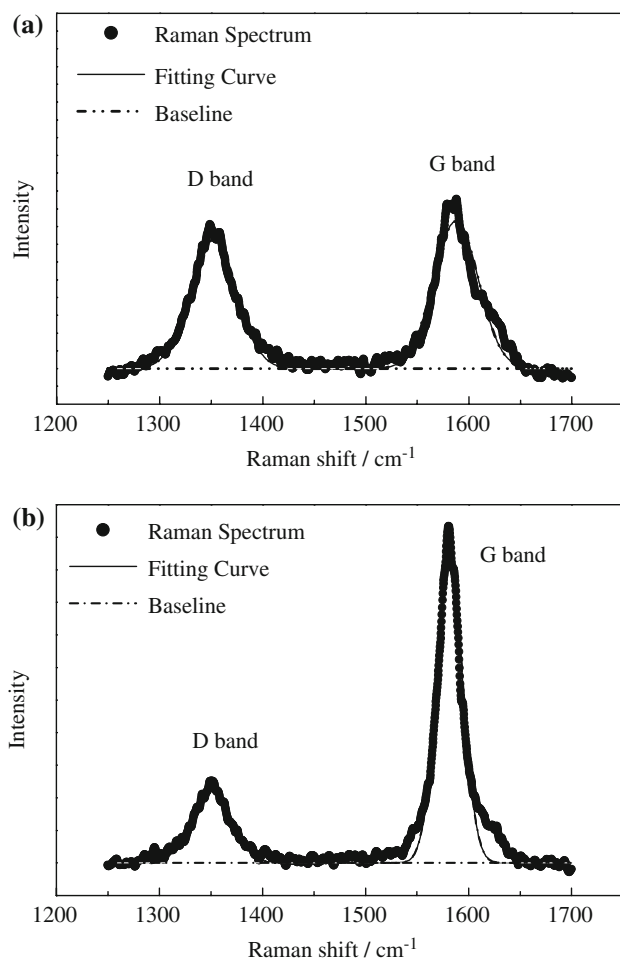


Fig. 2 Raman spectra of carbon fibers prepared from untreated and iodinated SF carbonized at 1400 °C for 12 h: (a) untreated specimen, (b) iodinated specimen

specimen, the C, H, N, and O contents were ca. 90, 6, 0.3, and 3 mol%, respectively. After iodine treatment, the elemental compositions were ca. 93, 5, 0.3, and 2 mol%, respectively. The results indicated that carbon contents were increased and the ratio of carbon to oxygen was maximized after iodine treatment.

Figure 5 shows the carbon yield of untreated and iodinated SF fibers at different temperatures. The weight residue percentages of untreated SF carbonized at 800, 1000, 1200, and 1400 °C were ca. 29, 28, 24, and 23 wt%, respectively. After iodine treatment, the carbon yields

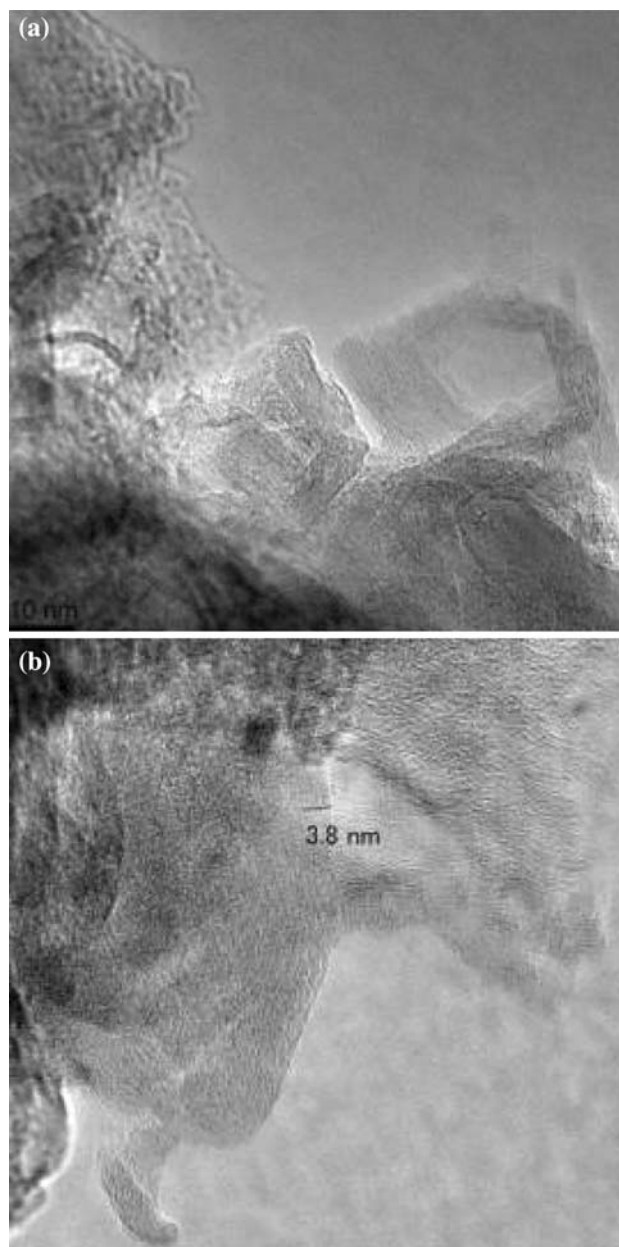


Fig. 3 TEM images of carbon fibers prepared from untreated and iodinated SF carbonized at 1400 °C for 12 h: (a) untreated specimen, (b) iodinated specimen

considerably increased and reached up to ca. 36, 31, 29, and 28 wt%, at 800, 1000, 1200, and 1400 °C, respectively. It was confirmed that iodine could not be detected

Table 1 Structural parameters of carbon fibers prepared from untreated and iodinated SF carbonized at 1400 °C for 12 h determined by Raman spectroscopy

| Specimen | G band | | D band | | I_D/I_G |
|--------------|-----------------------------------|--------------------------|-----------------------------------|--------------------------|-----------|
| | Peak position (cm ⁻¹) | FWHM (cm ⁻¹) | Peak position (cm ⁻¹) | FWHM (cm ⁻¹) | |
| Untreated SF | 1587 | 51 | 1350 | 53 | 0.89 |
| Iodinated SF | 1581 | 30 | 1350 | 45 | 0.29 |

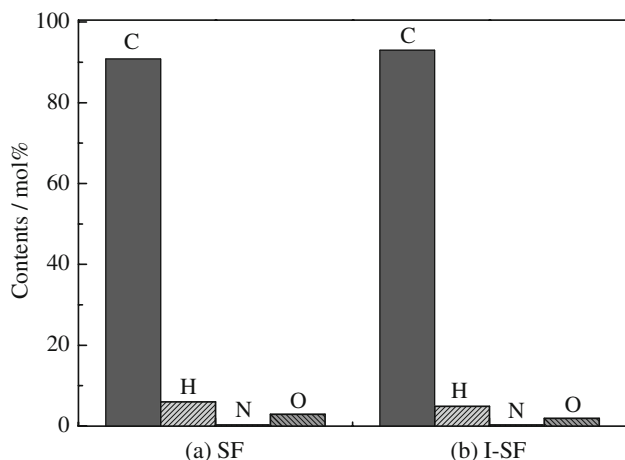


Fig. 4 Elemental composition of carbon fibers prepared from untreated and iodinated SF carbonized at 1400 °C for 12 h: (a) untreated specimen, (b) iodinated specimen

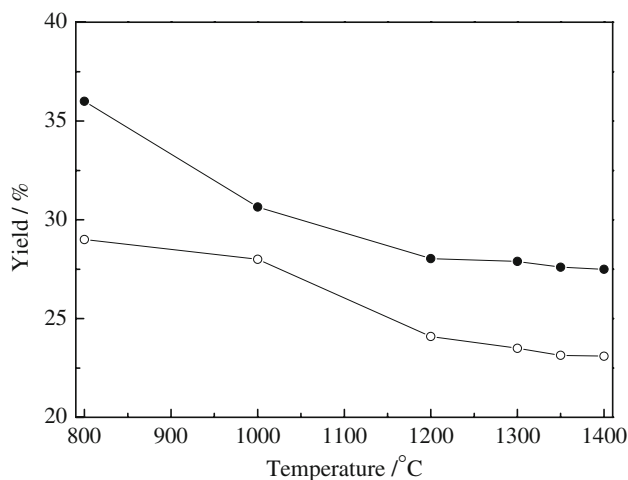


Fig. 5 Carbon yield of untreated and iodinated SF fibers obtained at different heating temperature: (open circle) untreated specimen, (filled circle) iodinated specimen

in the specimen after carbonized at different temperatures. Considering these results, iodine treatment seems an effective process to increase carbon yield of SF fibers at higher temperature.

Conclusions

The effects of iodine treatment on the carbonization and graphitization characteristics of *B. mori* SF fibers were studied. Prior to heating, SF fibers were treated with iodine vapor at 100 °C for 12 h. Untreated and iodinated SF fibers were carbonized to different temperatures, 800, 1000, 1200, and 1400 °C in a tubular furnace under an Ar flow under a multi step carbonization process, which was

defined based on the optimum thermal degradation rate of silk. WAXD measurement suggested that both untreated and iodinated SF fibers showed amorphous structure carbonized to 1200 °C. After carbonization at 1400 °C for 12 h, a graphite-like structure was obtained. In case of iodinated SF, the (002) peak was more visible, which suggests that iodine treatment has influenced SF molecules to build a graphite-like structure. Raman spectroscopy and TEM observation showed that the graphite-like layers in the SF fibers became more ordered after iodine treatment. The carbon yield obtained at higher temperature (1400 °C) after iodine treatment was higher, ca. 28 wt%, than that of untreated SF (cf. ca. 23 wt% of carbon yield for untreated SF).

Acknowledgements This work was supported by The Global COE Program and Grant-in-Aid for Scientific Research program by the Ministry of Education, Science, Sports and Culture of Japan. The authors gratefully thank Professor Fujio Okino, Dr. Yoshiyuki Hattori, and Mr. Hisatoshi Koshikawa, Faculty of Textile Science and Technology, Shinshu University, Japan, for their help in TEM measurements.

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