Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Multilateral Characterization of Recombinant Spider Silk in Thermal Degradation

Anh T. N. Dao[1], Koyuru Nakayama[1], Jun'ichi Shimokata[1,2], Toshiaki Taniike[*,1]*

[1]School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, JAPAN

[2]Spiber Inc., Tsuruoka, Yamagata 997-0052, Japan

*Corresponding author:

Toshiaki Taniike: Associate Professor, School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, JAPAN. Phone: +81-761-51-1630. Fax: +81-761-51-1635. E-mail: taniike@jaist.ac.jp.

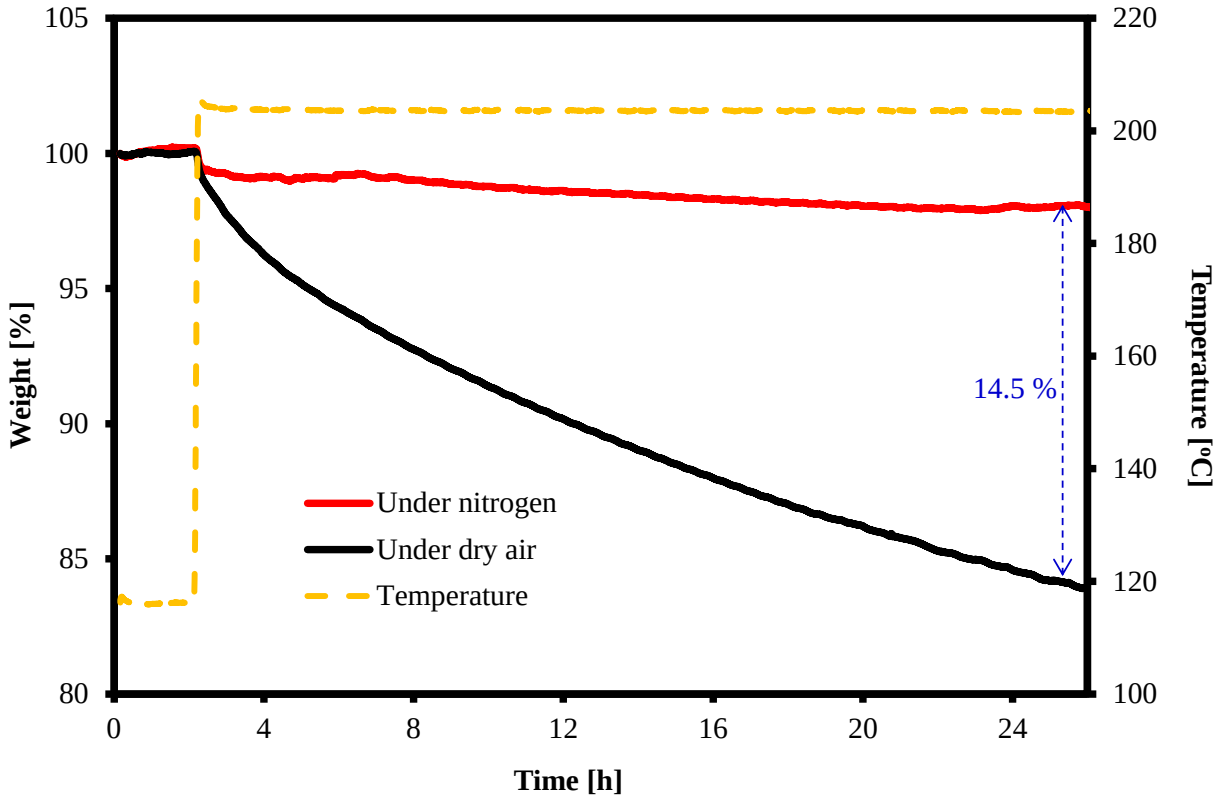

Figure S1. TGA curves of silkworm silk powder in an isothermal mode at 110 °C for 2 hours to remove free water and at 200 °C for 24 hours to promote the degradation.

Figure S1 shows TGA curves of silkworm silk under nitrogen and dry air. The temperature was brought to 200 °C and kept for 24 hours. Under N_2, the mass loss around 7.8 wt % was detected. The mass loss became much greater (22.3 wt %) under dry air. It is well known that the auto-oxidation (radical-based oxidation) of polymer exhibits a similar TGA behavior, i.e. significant mass loss due to the decomposition of a polymeric backbone in oxidative atmosphere.

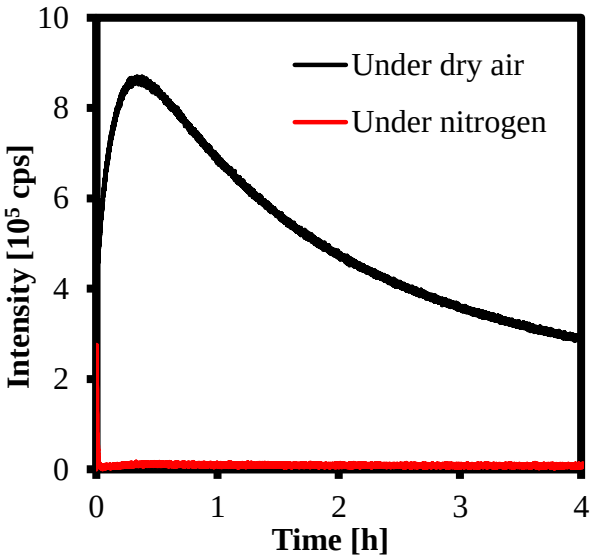

Figure S2. Chemiluminescence profiles of silkworm silk powder at 200 °C under dry air and nitrogen.

Figure S2 shows the chemiluminescence results for silkworm silk under nitrogen and dry air kept isothermally at 200 °C. Strong chemiluminescence intensity under dry air proved the oxidation of silkworm silk at the time scale of hours. Meanwhile, the thermal treatment under nitrogen was free from luminescent reactions.

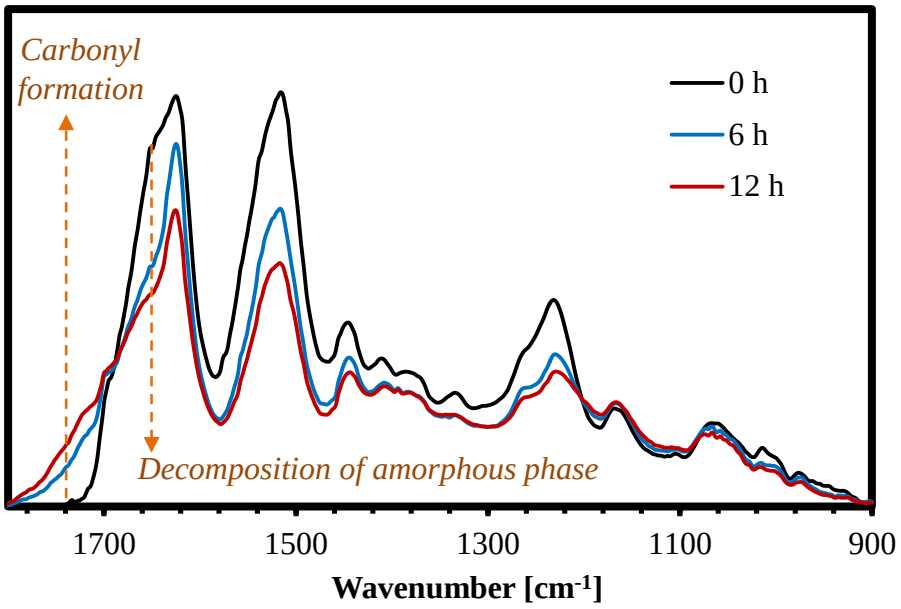

Figure S3. ATR-IR spectra for silkworm silk before and after degraded at 200 °C under dry air for 6 and 12 hours.

From Figure S3, it is clear that the amide I–III regions went through major changes during aging. The absorbance intensities of amide I, II dramatically decreased, and the amide III band mostly vanished. Contrary, a left tail of the amide I band developed into a shoulder along the aging around 1800–1700 cm^{-1}. The position of the shoulder was centered at ca. 1760 cm^{-1}, which is reasonably assigned to carbonyl species as one of the most plausible oxidation products. Importantly, the present result clarified that the thermal degradation of silkworm silk exhibits the formation of a similar oxidation product to recombinant spider silk.

In summary, the TGA, chemiluminescence and ATR-IR results of silkworm silk showed strong consistency to the conclusions obtained for recombinant spider silk. Therefore, we can conclude that the analytical approach and the characterization results can be applicable for studying the degradation of other silk materials.