THERMAL PROPERTIES AND STRUCTURE CONFORMATION ON SILKWORM SILK FIBRE

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Abstract

Silkworm silk fibre extracted from cocoon has been well recognized as a promising material for bio-medical engineering applications because of its superior mechanical and bioresorbable properties. Degumming is a surface modification process which allows a wide control of the silk fibre's properties, making the fibre possible to be used for the development and production of novel bio-composites with unique/specific mechanical and biodegradable properties. In this paper, the thermal properties and secondary structure were investigated to study the effects of distilled boiling water degumming. It was found that the degumming time had a little effect on the thermal decomposition properties and secondary structure of the silk fibre.

Introduction

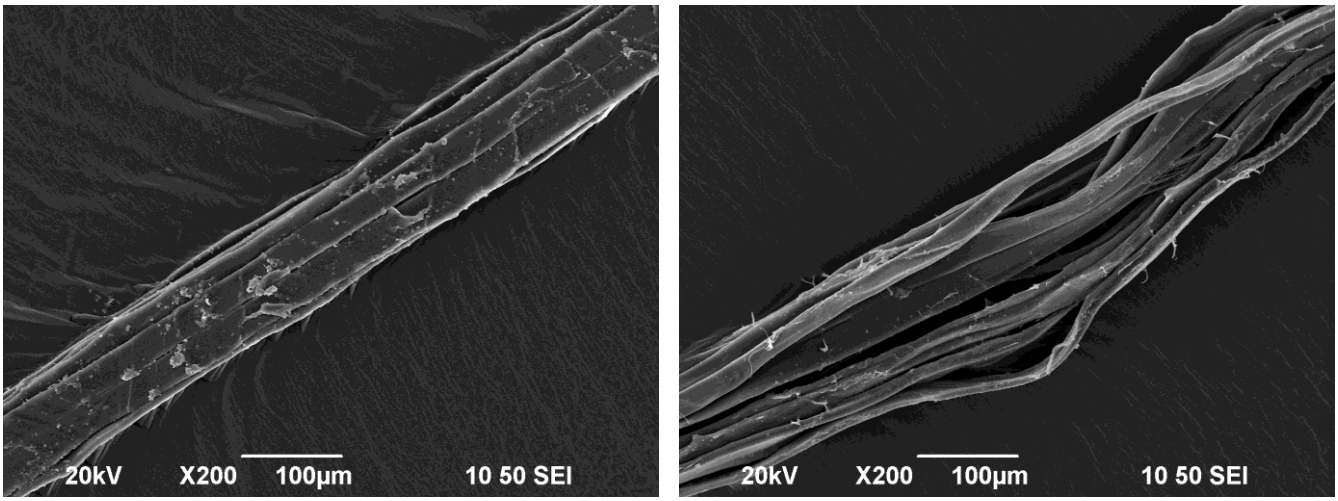
The protective functions of glue-like protein called sericin on silk fibroin surface against microbail degradation, animal digestion, and other damaging processes include: (1) oxidation resistance, (2) antibacterial function, (3) UV resistance and resistance against light damage etc [1-3]. Pre-processing of silk commonly known as degumming is an essential process to obtain a long and continuous fibre for sericin removal. The principle of degumming process is using water to hydrolyze the sericin, breaking the peptide linkage of amino acid into small molecules and solving it in water or other degumming solution such as soap, alkali, synthetic detergents, or organic acids [4].

However, degumming could affect the tensile properties of silkworm silk shown as table 1[5-6]. It was also reported to have a significant effect on the surface characteristic of the fibre (Figure 1) [6]. In addition, when producing silk fibre reinforced composites, hydrophilic sericin was found to cause poor interfacial bonding with polymer because of the

incompatility. The efficiency of stress transferred between resin and fibre decreased from the weak interfacial regions and thus, their tensile and flexural strengths decreased [7].

Table 1. Load and Elongation at break of the Tussah silk fibres pre-treated at different temperatures.

Degummed time (min)	0	15	30	45	60
Load (N)	0.35	0.38	0.24	0.23	0.18
Elongation(mm)	5.6	5.9	4.9	4.7	3.8



(a) (b)

Figure 1. Surface of (a) raw silk fibres and (b) degummed silk fibre.

Silkworm silk fibre is a renewable protein biopolymer which is not only valuable in the textile industry, but also useful for medical application including sutures and gauzes for treating the skin wound because of its superior mechanical properties and biocompatibility [8-10]. However, sericin is considered to be the main inhalant allergen in silk sensitive persons [11]. The antigenic properties of silk are related to the sericin [9-10]. It will cause systemic anaphylaxis, localized reactions and asthma. Therefore, removing sericin is an important step for silk fibres applied to the medical application. It has not been well understood that how the boiling water affects the thermal properties of tussah silk fibre during the degumming process. In this paper, the thermal properties and structures of the degummed tussah silk fibres under different treated conditions as compared with undegummed fibre.

Material and experiments

Tussah silk fibre was supplied by Ocean Verve Ltd., Hong Kong. The fibres were cut into 200 mm and placed in a 100 mL breaker for preparation of degumming treatment, and sufficient distilled boiling water was added to completely immerse the fibres. The beaker with the fibres was heated in a hot water bath for 10 minutes, 30 minutes, 45 minutes and 60 minutes respectively. Afterward the boiled fibre were washed with distilled water and dried immediately at 80^{o}C for 8 hours. Raw silk fibre samples, was referred as untreated control samples, were dried at 80^{o}C for 8 hours similarly.

Differential scanning calorimetry (DSC) curves were obtained with a thermal analysis instrument at a heating rate of 10 ^{o}C/min and a nitrogen gas flow rate of 50 mL/min. approximately 6-10 mg of samples obtained at different degummed parameter was sealed in aluminium pans. The experiments were performed in nitrogen atmosphere.

Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 with heating rate of 20.0 ^{o}C/min up to 600 ^{o}C. The experiments were performed in nitrogen atmosphere. Silk fibre is normally stable up to 140 °C and its thermal decomposition temperature is greater than 150 °C.

Fourier transforms infrared (FTIR) spectra were obtained from spectrometer (Perkin Elmer16 PC FTIR spectrophotometer) in the spectral region of 2000-600 cm^{-1}. Before testing, the fibre was mixed with KBr powder and cold-pressed into a disk suitable for FTIR measurement. For all measurement, the thickness of specimen was controlled at 5 um.

Result & discussion

DSC curves of tussah silk fibre degummed with different length of time are compared with that of control sample in figure 2. The shapes of hear flow curves appeared to be little affected by the degumming time [12]. Silk fibre displayed two broad and large endothermic peaks which are at around 100°C, due to the loss of moisture, and about 365°C, attributed to thermal degradation of a well-oriented β-sheet crystalline conformation respectively. The endotherm peak at about 225°C is attributed to the molecular motion within the α-helix crystals, while the exotherm peak at about 270°C can be attributed to the crystallization during heating by forming the β-sheet structure from a random-coil conformation.

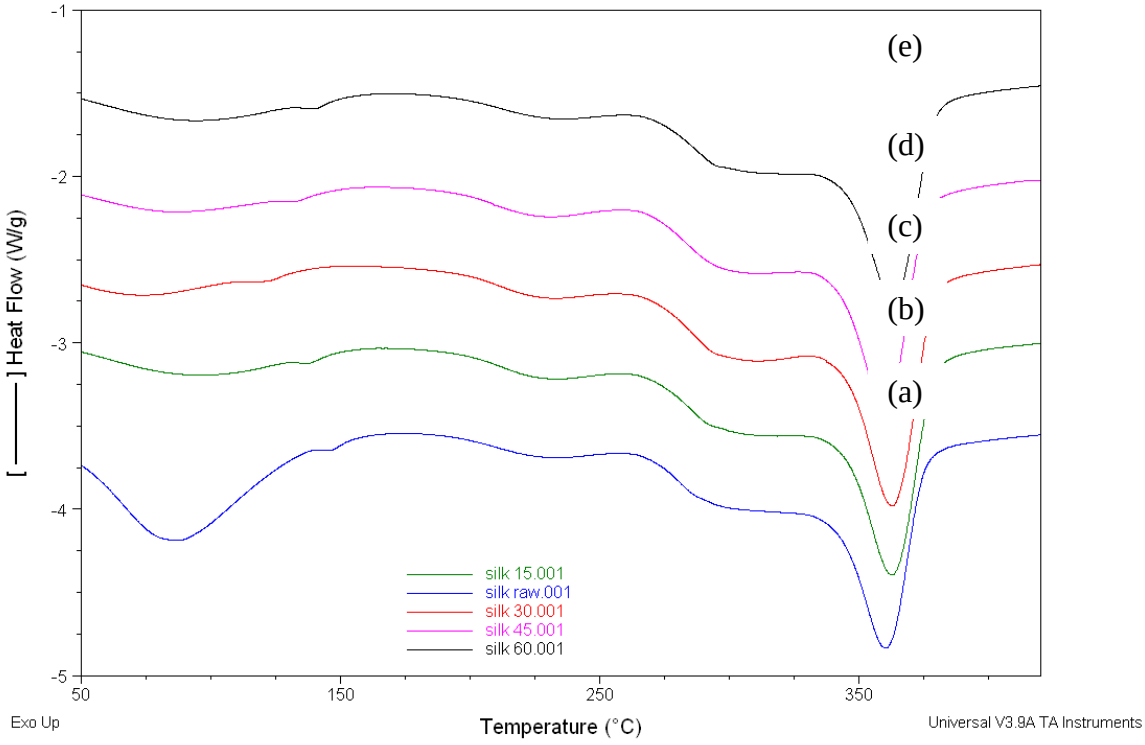


Figure 2. DSC curves of tussah silk fibres degummed for
(a) 0 minute (control sample), (b) 15 minutes, (c) 30 minutes,
(d) 45 minutes and (e) 60 minutes.

TGA curves of silk fibre are shown in figure 3. Different type of silk fibres exhibited different thermal degradation behaviours. It is mainly related to the polymorphs of crystalline structure and amino acid composition. For example, it was reported that thermal decomposition of B. mori fibre took place in a single step, but tussah silk fibre underwent several steps [13]. The TGA curves can be divided into three regions, characterized by evident different mass loss rates. The initial weight loss below 110 ^{o}C is attributed to the evaporation of water, and is follow by nearly constant weight from 110 ^{o}C to 170 ^{o}C. The very low mass loss observed in the second stage range from 170 ^{o}C to 275 ^{o}C can be attributed to the loss of other low temperature volatile species. The third loss from 275 ^{o}C to 390 ^{o}C is associated with the breakdown of side chain groups of amino acid residues as well as the cleavage of peptide bonds of tussah silk fibre [14-16].

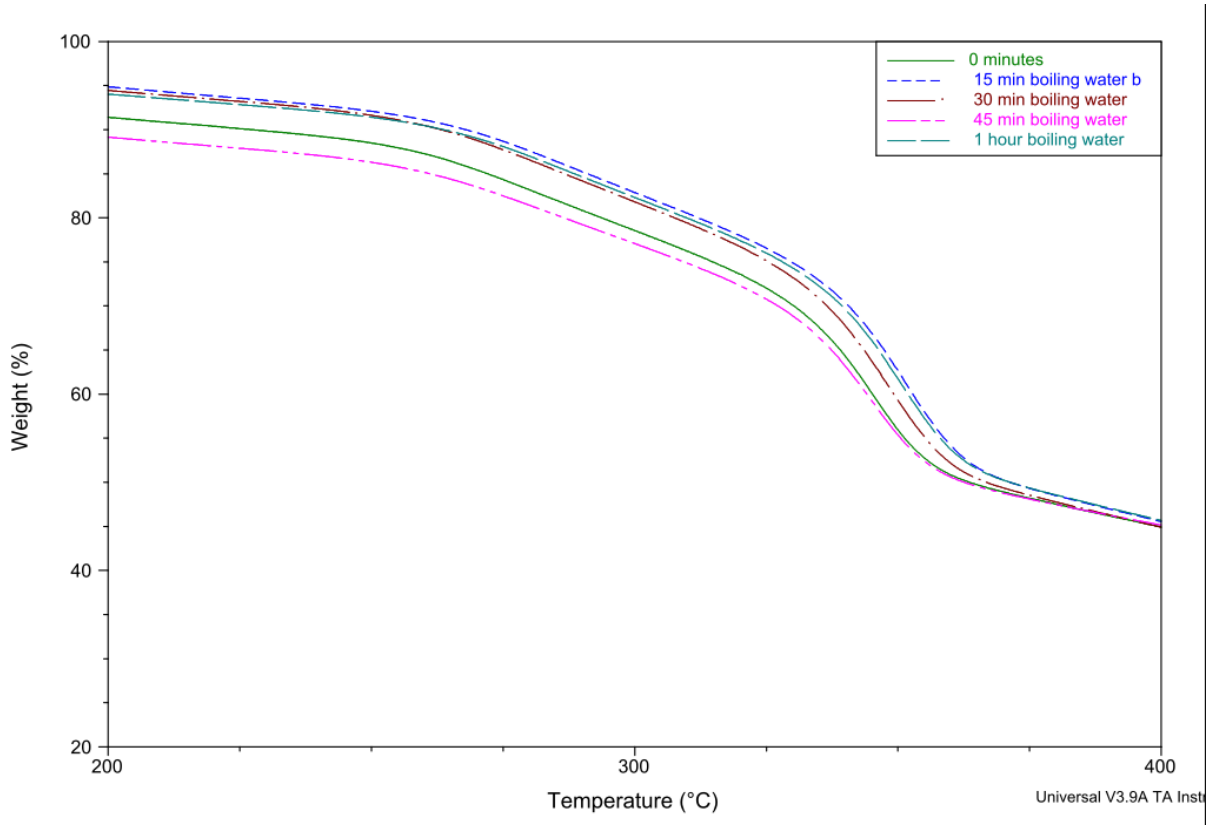


Figure 3. Thermogravimetric curves of the silk fibres degummed for (a) 0 minute (control sample), (b) 15 minutes, (c) 30 minutes, (d) 45 minutes and (e) 60 minutes.

The differential weight loss (*dW*/*dT*), DTG curves provide clear evidence for the above three degradation steps in figure 4. The maximum degradation temperature of each step was obtained at about 200^{o}C, 280^{o}C & 350^{o}C, respectively. However, both TGA and DTG curves of the degummed fibres did not differ significantly from those of the control sample, indicating that the water boiling treatment appears to have little effect on the thermal decomposition behaviour. The results from TGA matched with the DSC results. The beginning of weight loss occurred in the same temperature range of the endo/exo transitions recorded by the DSC traces [17].

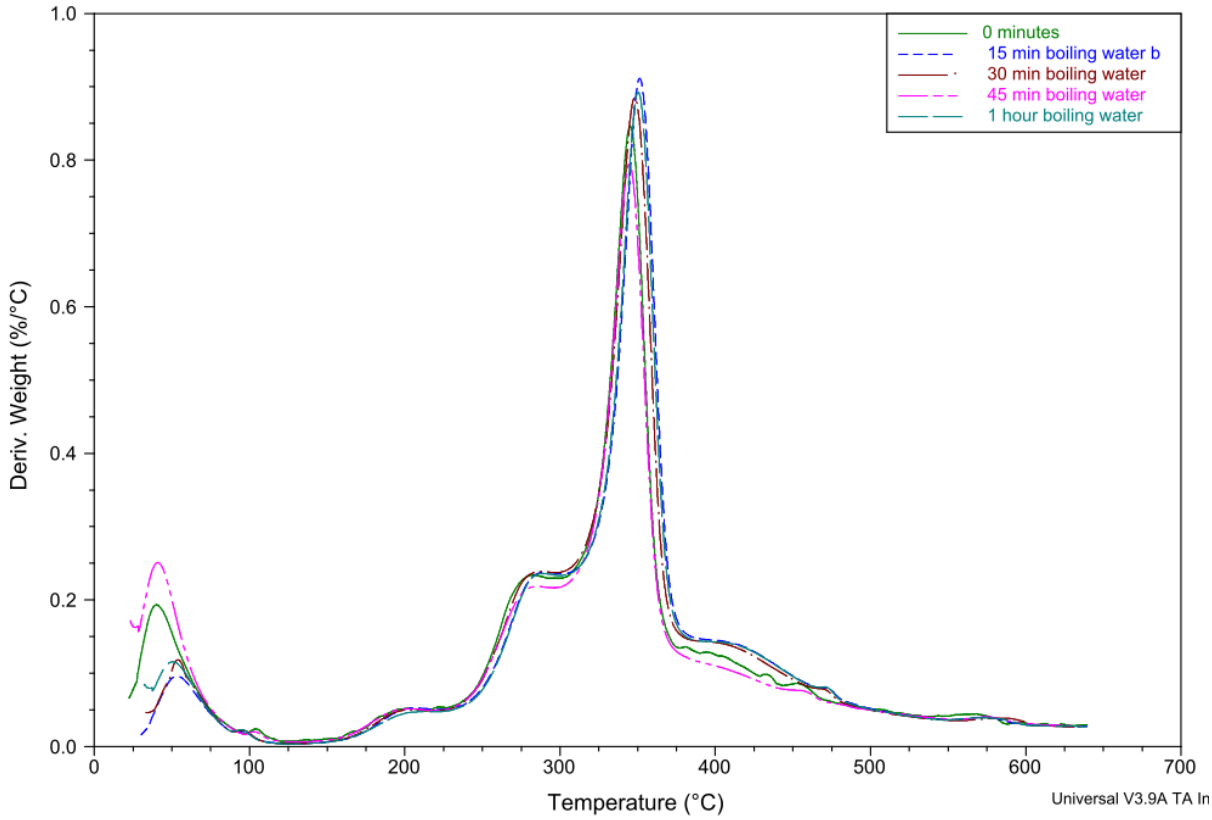
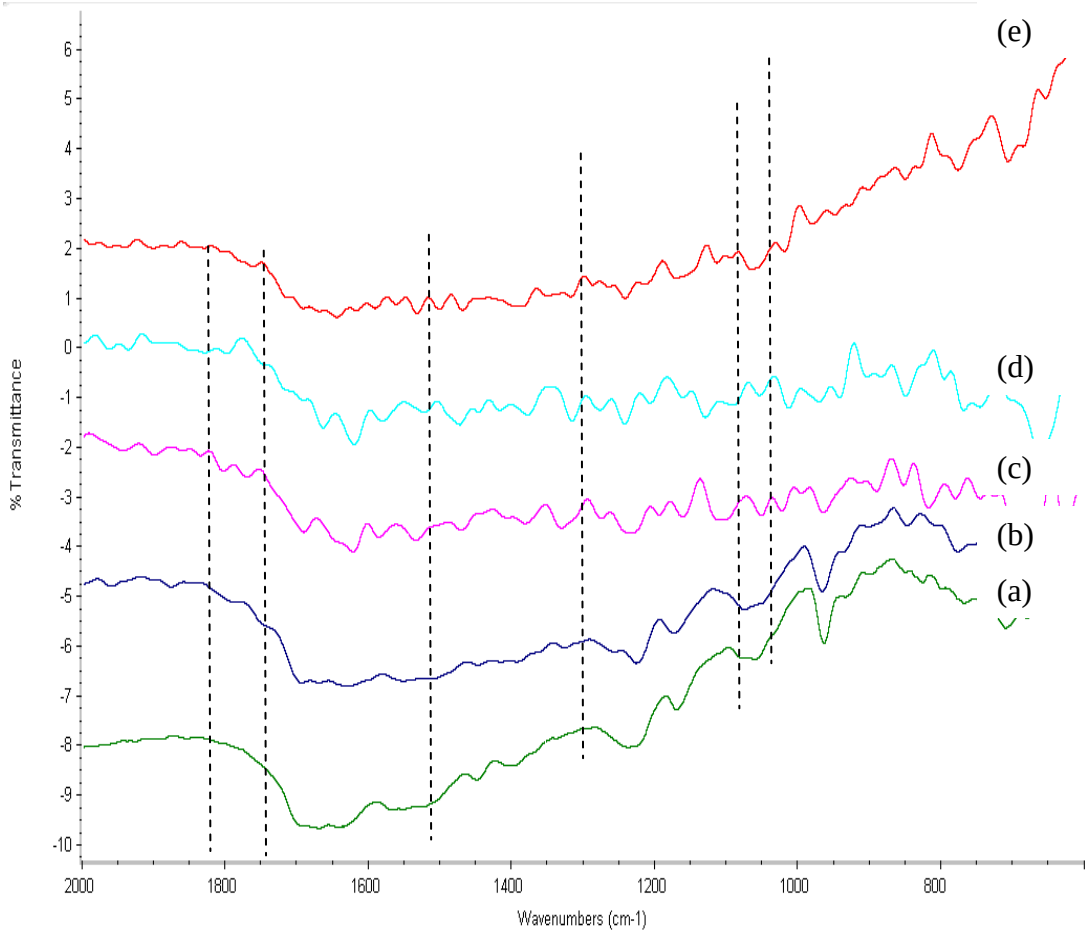


Figure 4. DTG curves of the tussah silk fibres degummed for (a) 0 minute (control sample), (b) 15 minutes, (c) 30 minutes, (d) 45 minutes and (e) 60 minutes.

In an attempt to examine whether the boiling water degumming induced the structure changes of the silk fibre, the secondary structure of all types of silk fibre samples were investigated using. Amide bands of FT-IR spectra which are known to be sensitive to the molecular conformation of silk fibre [15]. Figures 5 shows the FTIR spectra of all silk fibres degummed for different time period. All samples showed similar and strong bands at 1516 cm-1 (amide II), 1235 cm^{-1}(amide III), 965 cm^{-1}(amide IV), and 695 cm^{-1}(amide V), assigned to the β-sheet, and 1651 cm^{-1}(amide I) and 621 cm^{-1}(amide V), assigned to α-helix respectively. The similarity in TIR spectra implies that the molecular conformation of degummed fibres did not change and they assume to both of β-sheet structure and random coil α-helix conformation [18].



Figures 5. FTIR spectra of tussah silk fibre degummed for (a) 0 minute (control sample), (b) 15 minutes, (c) 30 minutes, (d) 45 minutes and (e) 60 minutes.

Conclusion

Pre-processing of silk commonly known as degumming is an essential process to obtain an ideal fibre because of its fibre structure. Silk degumming process scours the sericin and some impurities from silk fibres. Degumming could affect the tensile properties of silkworm silk. However, through the measurement of the thermal decomposition properties, secondary structure and surface morphology, the degumming has been shown to have little effect on the thermal properties and secondary structure of the silk fibre.

Reference

[1] Altman G.H., Diaz F & Jakuba C. Silk-based biomaterials. Biomaterials 2003: 24; 401-416.

[4] Meinel L, Hofmann S. the inflammatory responses to silk films in vitro and in vivo. Biomaterials 2005: 26; 147-155.

[5] Panilaitis B, Altman GH. macrophage responses to silk. Biomaterials 2003: 35; 3079-3085.

[6] Ho MP, Lau KT, Wang H. Characteristics of a Silk Fibre Reinforced Biodegradable Plastic. Composite Structures. Composites: Part B. 2011; 42: 117–122.

[7] Michal Z, Frantisˇek S. Unique molecular architecture of silk fibroin in the waxmoth, Galleria mellonella. Journal of Biological Chemistry 2001; 277(25) : 22639–22647.

[8] Atkins E. Silk's secrets. NATURE. 2003: 424.

[9] Osnat H., David PK. Spider and mulberry silkworm silks as compatible biomaterials. Composites: Part B 2007; 38: 324–337.

[10] Mondal M, Trivedy K. The silk proteins, sericin and fibroin in silkworm, Bombyx mori, Linn. - A review. Caspian J. Env. Sci. 2007; 5 (2): 63-76.

[12] Ping J, Huifen L. Tensile behavior and morphology of differently degummed silkworm (Bombyx mori) cocoon silk fibres. Materials Letters 2006; 60: 919– 925.

[13] Kurosaki S, Otsuka H. Fibroin allergy: IgE mediated hypersensitivity to silk suture materials. J Nippon Med Sch 1999:66(1);41-44.

[14] Kweon HY, Um IC & Park YH. Thermal behavior of regenerated Antheraea pernyi silk fibroin film treated with aqueous methanol. Polymer 2000; 41: 7361–7367.

[15] Freddi G, Monti P, Nagura M, Gotoh Y & Tsukada M. Structure and Molecular Conformation of Tussah Silk Fibroin Films: Effect of Heat Treatment. Journal of Polymer Science Part B: Polymer Physics 1997; 35(5): 841–847.

[16] Kweon H & Park YH. Dissolution and Characterization of Regenerated Antheraea pernyi Silk Fibroin. Journal of Applied Polymer Science 2001; 82: 750–758.

[17] Motta A, Fambri L, Migliaresi C. Regenerated Silk Fibroin Films: Thermal and Dynamic Mechanical Analysis. Macromolecular Chemistry and Physics 2002: 203(10-11): 1022-1352.

[18] Li M, Tao W, Kuga S & Nishiyama Y. Controlling Molecular Conformation of Regenerated Wild Silk Fibroin by Aqueous Ethanol Treatment. Polymers for Advanced Technologies 2003; 14(10): 694-698.