EFFECT OF DEGUMMING ON TUSSAH SILK FIBRE

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Abstract

Silk fibre is well recognized as an outstanding material for bio-medical engineering application because of its superior mechanical and bioresorbable properties. However, when producing silk fibre reinforced polymer composites, hydrophilic sericin has been found to cause poor interfacial bonding with polymer. Besides, sericin on the fibre surface is a major cause of adverse problems with biocompatibility and hypersensitivity to silk for implant application. Therefore, certain treatment should be proposed for sericin removal. Degumming is a surface modification process which allows for a wide control of the silk fibre's properties, making silk possible to be used for the development and production of novel bio-composites. In this paper, a cleaner and environmental friendly surface modification technique of tussah silk was under investigated. The effectiveness of parameters of degumming on tussah silk such as surface purity, degumming time and temperature is discussed. The evaluation of the data was carried out through the measurement of the tensile properties and surface morphology of the samples. The findings of this research provide an environmental friendly degumming method which is one of the most important steps on preparation of silk fibre reinforced composite.

1. Introduction

The silkworm silk fibre is composed of fibroin and sericin [1]. The fibroin fibre itself is a bundle of several fibrils with a diameter of 1μm. A fibril contains 15nm wide microfibrils. Microfibrils are packed together to form the fibril bundle and several fibril bundles produce a single strand [2]. These fibroins are encased in a sericin coat, a family of glue-like proteins that hold fibroins together to form the composite type of fibres of the cocoon case [3]. Sericin is amorphous in nature and acts as binder to ensure the structural integrity of the cocoon.

Silk fibre is utilized for bio-medical engineering application because of its superior mechanical and bioresorbable properties. Silk fibres as sutures for human wound dressing have been used for centuries [4]. Recently, regenerated silk solutions have been used to form a variety of biomaterials, such as gels, sponges and films, for medical applications [5]. Moreover, silk has been exploited as a scaffold biomaterial for cell culture and tissue engineering in vitro and in vivo [6]. Nevertheless, a long and continuous fibre can only be reeled from the cocoon after the adhesive sericin coating has been removed. Besides, when producing silk fibre reinforced composites, hydrophilic sericin has been found to cause poor interfacial bonding with polymer because sericin hinders the bonding between the fibre and matrix in the composites, and thus the efficiency of stress transferred between resin and fibre decreased from the weak interfacial regions [7].

Besides, sericin on the fibre surface is a major cause of adverse problems with biocompatibility and hypersensitivity to silk for the implant application. Therefore, certain treatments should be proposed for sericin removal. Degumming is a surface modification process which allows for a wide control of the silk fibre's properties, making silk possible to be used for the development and production of novel bio-composites. Sericin removal requires thermo-chemical treatment of the cocoon in a process conventionally known as degumming [1]. However, degumming weakens at least one type of non-covalent interaction of core fibroin, such as hydrogen bonds and Van der Waal's bonds. Therefore, a balance between the degumming ratio of the fibres and the preservation of mechanical properties is a critical topic. The findings of this research provide an environmental friendly degumming method which is one of the most important steps on preparation of silk fibre reinforced composites. In this paper, cleaner and environmental friendly surface modification techniques of tussah silk were investigated. The effectiveness of degumming parameters on tussah silk such as degumming time and temperature depended on different methods was discussed. The evaluation of the data was carried out through the measurement of the weight loss, strength, and elongation of the silk composites.

2. Material Preparation and Experiments

Tussah silk fibre was supplied by Ocean Verve Ltd., Hong Kong. The shape of ordinary tussah silk fibre is in a flat triangular form. Silk fibres were separated carefully from a bundle. Special care was taken to avoid stretching the fibre plastically during the whole experiment process. Extracted silk fibres were cut into 200 mm and placed in a 100mL breaker for the preparation of degumming treatments, and sufficient distilled boiling water was added to completely immerse the fibres into the water. The beakers with the fibres were heated in a hot water bath for 10 minutes, 30 minutes, 45 minutes and 60 minutes respectively. Afterward the hot water treated fibres were washed with cold distilled water and dried immediately at 80°C for 4 hours. Raw silk fibre was referred to as an untreated sample dried by 80°C for 4 hours similar to other hot water treated fibres. Each fibre as sample was mounted on cardboard frames by tapes and removed any slack without stretching the specimen. The cardboard frame was cut with scissors through the discontinuous line as shown in the figure before starting the experiment. The diameter of center hole was 100 mm. All samples must be well aligned to the loading direction to avoid any mis-measurement of the strength of fibres.

All measurements were carried out on an MTS Alliance RT/10 materials testing machine at a crosshead speed of 60 mm/min and under standard environmental conditions (20 °C, 60% relative humidity). The samples were tested according to ASTM D 3822. Some samples were further coated by gold for scanning electron microscope (JEOL Model JSM-6490) imaging.

3. Results and Discussion

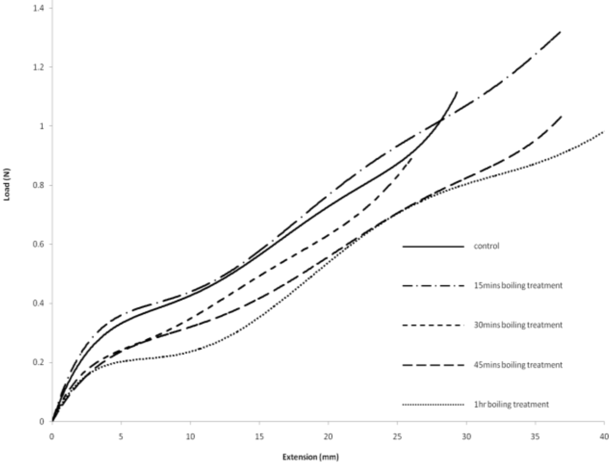


Figure1. Load-displacement curves of control and degummed tussah silk fibres.

Figure 1 shows the load-displacement curves obtained from the tensile test of tussah silk fibres with the gauge length of 100 mm. Tussah silk fibres which were degummed for 15 minute in the hot water can support a much higher load as compared with other samples. Table 1 summarizes the average F_p (force) and ε_p (elongation) at the elastic limit point of all samples (extracted the results from 10 samples at each type of hot water treated temperature). Jiang et al. has suggested that the degumming process has two principal quantitative effects on the force-displacement plots which include initial slope and the elastic limit (i.e. yield point) [8]. For the sample degummed for 15 minutes, the initial slope is steeper as compared with the result of the raw fibre. However, for the samples degummed over 15 minutes, their initial slope and the elastic limit (i.e., yield point) are lower than that of the raw fibre. Based on the results of all curves, it is clear to see that the fibres degummed over 1 hour cause the substantial decrement in their elastic region (by 50% as compared with the sample degummed for 15 minutes) because of the damages of the fibroins. A tussah silk fibre exhibits three regions including an initial linear elastic region (A), a yield region (B), and a hardening region (C) with turning as the load increases to the maximum in its stress-strain curve. Figure 2 shows the stress-strain curves of all types of samples. The sigmoidal “rubber like” shape of the curves obtained from the experiments matches the result obtained from Zhang et al. [9].

Table 1. Load and Elongation 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

Table 3 shows all tensile parameters of the samples including elastic modulus E (initial modulus), slope of yield region, slope of hardening region, the strain at the proportional limit, the tensile strength and the strain at breaking. Tables 1 & 2 show that the samples which were degummed for 15 minutes are the best in term of the tensile strength among the samples. For the effect of degumming time on tensile strength of silk fibre, it is shown that fibres degummed for 15 minutes are more compliant and have better tensile strength properties than that of other samples. For the samples being degumming over 15 minutes, their initial tensile modulus, slope of yield region, slope of hardening region, strain at the proportional limit, tensile strength and strain breaking and yield points for degummed samples drop dramatically and start to decrease gradually when the degumming process is taken over 30 minutes. According to the results shown, it can be concluded that by increasing the time for degumming, the amount of sericin removal increase, and causes the damage of the fibroins eventually.

Certain factors whereby degumming could influence tensile properties of silkworm silk including, 1) fibre scatter, 2) sericin removal and 3) molecular changes. Sericin removal contribute the cross sectional area of the fibres reduction significantly. As sericin acts as the glue to bind up all fibroin filaments together, degumming would cause the removal of sericin which makes the fibres in a loose pack form. Therefore, the diameter of the fibre increases after degumming. One of the reasons of the strength diminution of the tussah silk fibre is their twisting character of the filaments. After degumming, the filaments of fibres, due to the missing of binding agent (i.e. sericin) would potentially align towards the loading direction. Thus, a friction in-between the filaments were reduced. In such case, the fibre can take a larger portion of tensile load instead of friction. The fibres degummed after 15 minutes have less strength compare with the control sample. The strength of the fibre degumming for 15 minutes increases because of the decrease of the cross sectional area. As load-bearing capacity of sericin is very small compared to that of fibroin, remove the sericin which represents reduce the cross sectional area and increase the effective cross sectional area.

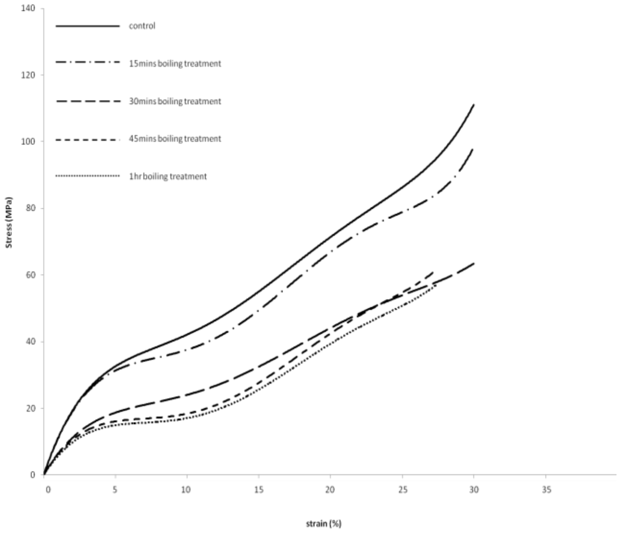


Figure 2 Stress-strain curves of tussah silk fibres.

Molecular change is one of the consequences of degumming which infer the force-displacement curves of control and degummed silk. Degumming weakens at least one type of non-covalent interaction, such as hydrogen bonds. However, most natural fibres owe their strength to hydrogen bonding. Hydrogen bonding plays an important role in the secondary, tertiary, and quaternary structures of proteins. This interpretation is consistent with the fact that water act as a plasticizer [10] by intra-molecular hydrogen bonding so that the displacements of penetrating amorphous regions and interrupting the inter- and protein chain segments and stress relaxation is increased.

Table 2 Summary of the tensile stress, strain, modulus, maximum force and elongation of the samples.

	Initial modulus (GPa)	Slope of yield region	Slope of hardening region	Strain at the proportional limit	Tensile strength (MPa)	Strain at breaking
Control	102.86	5.714	32	5.3	156.293	28.05
Degumming after 15 minutes	112	20	30	4.5	159.837	34.127
Degumming after 30 minutes	55	5.714	6.67	4	124.081	28.838
Degumming after 45 minutes	51.43	5	6.67	3.7	106.982	27.489
Degumming after 60 minutes	45.71	0.333	6.67	3	104.922	22.625

The tussah silk fibre obtained directly from the spinneret of silkworm is free from calcium oxalate crystals at micrometer size, which are usually observed on the undegummed cocoon silks. The micrometer-sized calcium oxalate crystals which are excretions by the silkworm and shown in figure 3 which same as finding from Fu et al. [11]. The surface morphology of degummed silk fibres using distilled boiling water for different period was under investigated by SEM and the SEM micrographs are illustrated in figure 4(a)-(e). The surface morphology of control samples is as shown in figure 4(a), the surface characteristic of the tussah silk fibre is fairly rough. This rough surface was clearly evident to large amount of sericin coating. The sericin appears as some partially non-uniform coating on the surface of the fibroins and various granulas and impurity deposits are visible in the vacant spaces in between fibroins. Figure 4a, the ordinary tussah silk fibre is not circular in cross section but its shape is in flat triangle. Each tussah silk bonds and comprises of many fibroin strands. The sericin coated fibroin strand itself is a bundle of several fibrils and the periphery of the silk fibroin strands coagulate many sericin particles irregularly [12].

Different surface morphology and fibre damage of the raw silk fibre and degummed silk at various conditions were observed among the SEM micrographs of the fibres. The micrographs of samples degummed for 15 minutes show good degumming result and no sign of destruction or damage on the surface of silk fibres (figure 4b). The fibre surface is greatly smooth, showing only very shallow longitudinal striations attributable to the fibrillar structure if the truly degummed silk fibres. After 30 minutes boiled samples free from non-uniform coating and any granulas and impurity. In some parts of the fibroin, sericin layers break away from the main fibre axis, leaving the clean fibroin appear to the surface. In micrograph 4 c-e was shown that surface of degummed silk fibre after 30 minutes, under this condition could almost completely remove sericin on the fibroin surfaces but some damages were observed when increasing the degumming time. The case get worse among the results as much more damages were observed from the sample which degummed after 60 minutes. The higher magnification of SEM examination of the tussah silk fibre shows that the individual silk fibroin strands were split off (figure. 5(a)). Fibrillation of some fibroin threads have also found (figure 5(b)). Moreover, based on figure 4 (a-e), it is found that the fibre diameter is increased gradually when extending of the degumming period. It is mainly because the binder (sericin) is dissolved into the water so that the fibroins disperse.

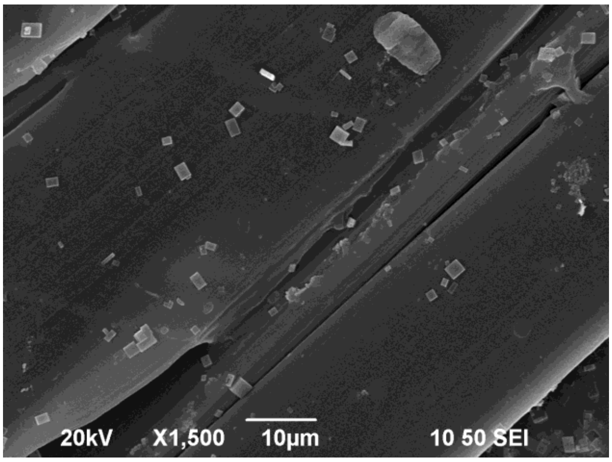
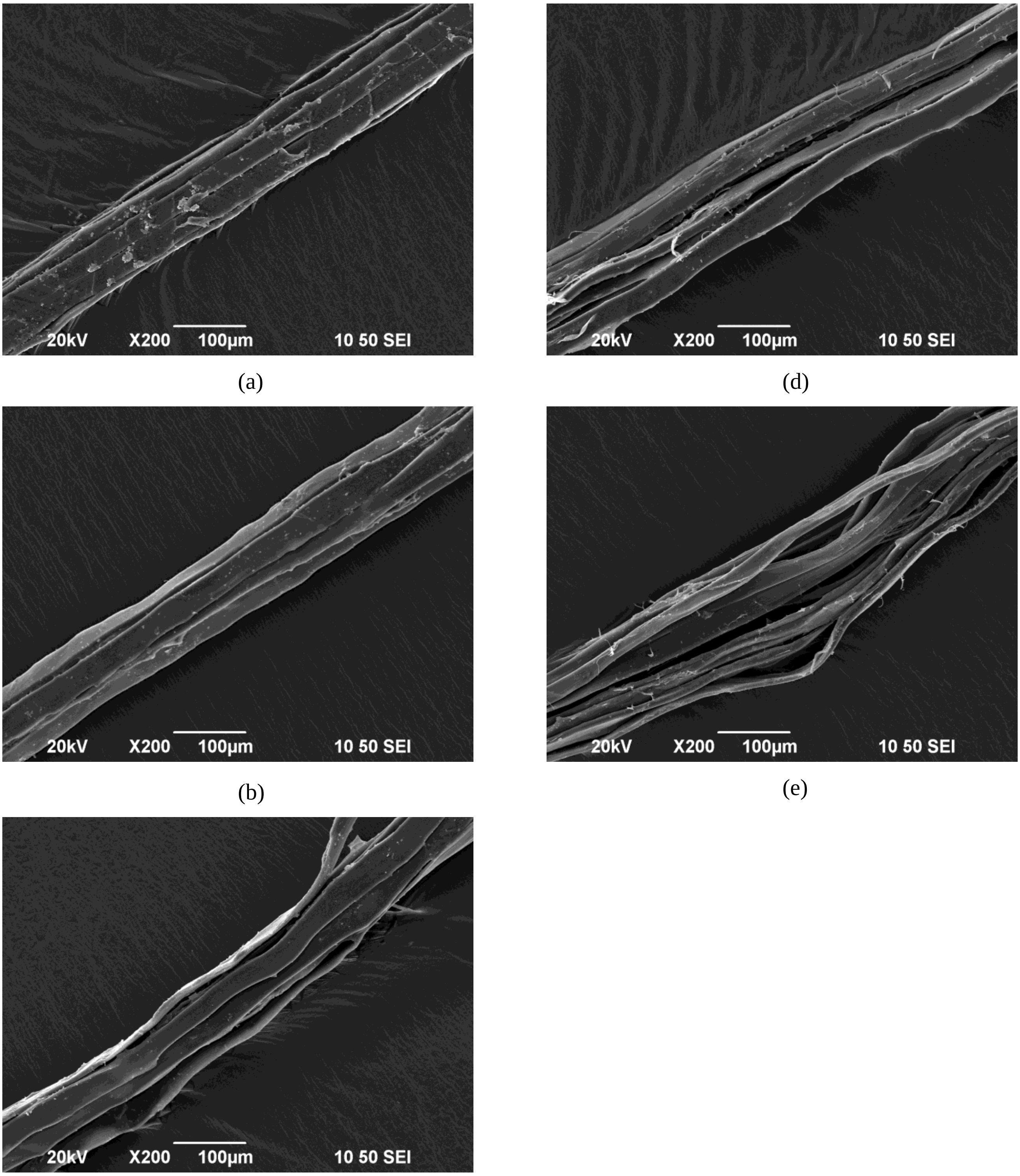


Figure 3. Micrometer-sized calcium oxalate crystals on the surface of tussah silk fibre.

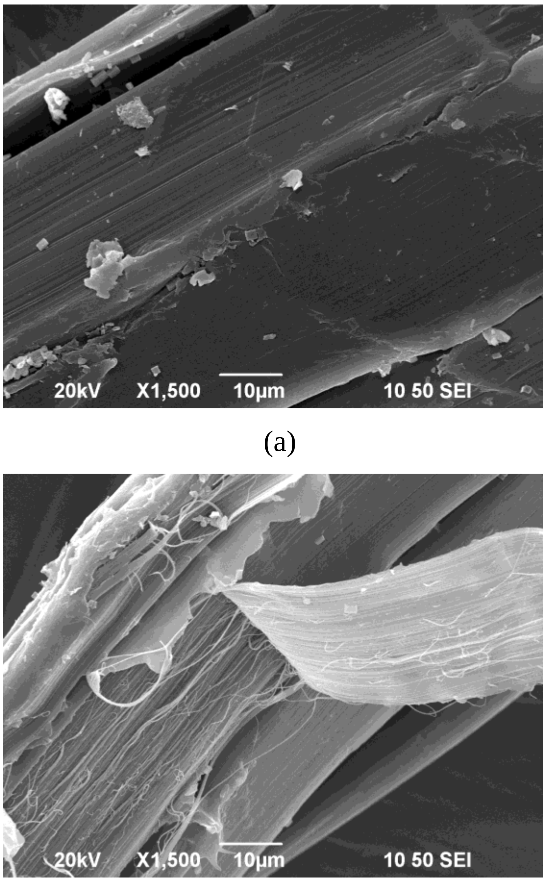


(a) (d)

(b) (e)

(c)

Figure 4. longitudinal surface morphologies of Tussah silk fibre degummed for (a) 0 minute (control sample), (b) 15 minutes, (c) 30 minutes, (d) 45 minutes, (e) 60 minutes.



(a)

(b)

Figure 5 (a) & (b). Typical defects of the degummed tussah silk fibre indicated by arrows.

4. Conclusion

Preprocessing of silk commonly known as degumming is an essential process to obtain an ideal fibre because of its modified fibre structure. Silk degumming process is scouring the sericin and some impurities from silk fibre. Through the measurement of the mechanical properties and surface morphology of the samples, the results show that using boiling water for degumming for 15 minutes obtain the maximum tensile strength, strain and modulus. As the major amino acids groups in sericin is hydrophilic, water and heat treatment destroying the hydrogen bonding of the sericin so that sericin dissolves into the water during the degumming process. From the SEM analysis, the micrograph show that all the impurities were removed and no damage on the surfaces can be found.

5.References

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