Properties of Industrial Thai Silks Reeled by Hand and by Machine

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Abstract

Three mulberry silk filaments from the local producers and one imported silk filament were analyzed for various properties. The properties of the silk filaments reeled by hand and by machine were compared. The properties assessed were whiteness and yellowness, fineness or denier, degumming weight loss, moisture content, relative density, birefringence, crystallinity, chemical composition, softening point, burning behavior, tenacity, resistance to sunlight, dye fixation, and resistance to acid, alkaline and bleaching conditions, according to the standard test methods. It was found that the hand reeled silks showed the lower values in whiteness, birefringence, crystallinity and softening point than those of the machine reeled silks. On the other hand, the hand reeled silks showed a higher denier and dye fixation. The local silks were found to have the higher values in denier, degumming weight loss, relative density, crystallinity, dye fixation, and resistance to alkali and bleaching agent than the imported Chinese silk.

Key words: **Thai silk, hand reeling, machine reeling, properties**

Introduction

There are various kinds of silk depending on source such as Thai silk, Indian silk, and Chinese silk. Thai silk filaments differ from those of other countries in many ways. They are usually soft but have a relatively coarse texture with uneven, slightly knotty threads (a unique property not found in other silks). Silk in Thailand can be classified into three types based on the silk worm species namely Thai silk worms, a mixed hybrid of Thai and foreign silk worms and mixed hybrid of foreign silk worms. These silk worms produce varying qualities and properties of silk filaments. In addition, the properties of silk filaments in Thailand have not really been investigated and characterized.

Asakura *et al.*[1] studied the structure of Bombyx mori silk fibroin using the solid state ^{13}C-NMR technique. As expected, the NMR spectra showed very sharp ^{13}C-NMR signals of the silk fibroin. These results indicated

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a fast segmental motion of the fibrous protein at a high molecular weight of 300,000. Nakamura et al.[2] investigated the thermal properties of the silk proteins in silkworms and found that water evaporated off as the temperature of the amorphous random-coil fibroin of Bombyx mori was raised to 100 °C. Intra- and intermolecular hydrogen bonds of the silk proteins were broken at the temperatures of 150-180 °C and the glass transition temperature was 175 °C. Silk sericin showed a glass transition temperature of 170 °C. The glass transition temperature of wild silk fibroins varied with the species of silkworm and ranged from 160-210 °C.

Annadurai *et al.*,[3] computed the crystal imperfection parameters and the shape of crystallites of varieties of silks (Chinese, Indian, and Japanese races) using the X-ray profile analysis, and observed the influence of these parameters on physical properties of the silk filaments. They found that silk filament having a higher crystal size value showed a higher tensile strength and percentage elongation at breaking point than other silk filaments. Sen and Babu[4-6] studied the properties of the Indian mulberry and non-mulberry silk varieties. They found that denier, moisture regain, dye uptake, and elongation of the cocoon's outer layer filament were higher than those of the cocoon's inner layer filament for all silk varieties while density, tenacity and modulus showed the opposite results. Mulberry silk had lower moisture regain but higher density and dye uptake than the non-mulberry silk which contained microvoids at the filament cross-section. However, the non-mulberry silk had a higher molecular weight than the mulberry varieties.

In this study, we attempted to determine the properties of three local silk filaments reeled by hand and by machine. In addition, an imported Chinese silk filament was also studied. All silk filaments were subjected to various tests to determine their characteristics and their chemical and physical properties. This scientific information is very important for various applications in textile industry.

Experimental

Materials

The three mulberry silk filaments used in this research were two varieties of mixed hybrids between the Thai race and Japanese or Chinese race known as Chul 4 and Chul 6, and one variety of a mixed hybrid between the Japanese and Chinese races known as Chul 1. These raw filaments were reeled from silk cocoons (bivoltine) by hand and by machine at Chul Thai-Agro Industries, Thailand and only inner layer silk filaments were used. For the hand reeling, each silk variety was reeled in water at 90 °C at a speed of 19 m/min, while a Nissan automatic silk reeling machine was used for machine reeling at a speed of 90 m/min and a temperature and pH of water of 30-32 °C and 6.5-7, respectively. In addition, an imported Chinese silk filament was provided by Jim Thompson Thai Silk, Thailand. It was reeled by machine and an inner layer filament was obtained All chemicals used in this research were of reagent grade and utilized without further purification.

Methods

Degumming

Raw silk filaments were degummed at Chul Thai Silk Co., Ltd. using 2-3 g/dm^3 sodium carbonate and 5-6 g/dm^3 nonionic wetting agent at a liquor-to-silk ratio of 30:1, at a temperature of 98 °C, pH 10 for 45 minutes in a degumming bath. Both raw and degummed silk filaments were assessed for their appearance, physical and chemical properties, according to the test methods shown as follows.

Characterization

Appearance, Cross-Sectional and Longitudinal Views

Silk filaments were observed visually for their general appearance such as color shade luster, smoothness, and cleanliness in a standard lighting cabinet VeriVide under a light source of daylight (D65). They were also observed for their cross-sectional and longitudinal morphology under a scanning electron microscope (SEM, model JEOL JSM-5410LV).

Whiteness

Each variety of silk filament was paralleled and tightly wrapped on a flat sheet and then was subjected to whiteness measurement according to the AATCC test method 110. The whiteness of the silk was measured using a Macbeth reflectance spectrophotometer (Color-Eye 7000).

Denier

Each filament was weighed and measured for its length and the fineness or denier was determined by multiplying 9,000 by the ratio of the filament weight in gram over the filament length in meter, according to ASTM D1425.

Degumming Loss

Each raw silk filament was conditioned, weighed and then degummed in a stainless steel container of the laboratory dyeing machine Ahiba Polymat using the same formulation as shown previously in the degumming section. It was then washed, dried and conditioned overnight before weighing it and calculating its percentage of the degumming weight loss, according to JIS L0844.

Moisture Content

The moisture content of the filaments was determined by first conditioning each sample overnight and then weighing it before and after drying at 105 °C in an infrared weighing balance (model AD-4715). Its moisture content (%) was calculated by multiplying 100 by the ratio of the different filament weights before and after drying over the filament weight before drying, according to ASTM D2654.

Relative Density

The relative density of the filaments was measured based on Archimedes' method[5] using a density test kit (Sartorius YDK 01) according to ASTM D3800. First, a one-inch long sample was immersed in water for at least 13 hours at room temperature, then weighed, pressed to remove excess water, weighed, dried at 110 °C, and weighed again. The relative density was then calculated according to the following equations.

$$V = M - S \quad (1)$$
$$B = W / V \quad (2)$$
$$Dr = (B/D_t) \times 100 \quad (3)$$

Where V = the sample volume, M = the sample weight after removing excess water, S = the sample weight when soaking wet, B = the sample bulk density, W = the sample weight after drying at 110 °C, D_r = relative density, D_t = theoretical density

Birefringence

Silk birefringence (Δn) was determined using the Beckeline method.[5] It was calculated from the difference between the refractive indexes of a single filament in parallel and perpendicular directions, compared with that of a chloronaphthaline and cetane mixture (refractive index = 1.55). Under a polarizing microscope, the refractive index of the mixture in which the Beckeline disappeared was taken as the refractive of the sample.

Crystallinity

Silk crystallinity was analyzed using an X-ray diffractometer (model D8 Advance Bruker). The Ni-filtered Cu-K_α (1.54 Å) radiation was used at 40kV and 40 mA. Silk filaments were scanned between 5 and 32° (2θ values) with a rate of 2 ° per minute, compared with their amorphous silks. Amorphous silks were prepared as references for each variety of silk by dissolving the degummed silks in solutions of ethanol, water, and calcium chloride at a ratio of 5:6:8, respectively and at a temperature of 50 °C for 60 minutes[5]. Then the non-dissolved portions were screened out and the dissolved amorphous samples were coagulated in water, dried and ground into a powder form. The percentage crystallinity of the silk filaments was determined according to equation 4.

$$\% \text{ crystallinity} = [1 - (A_a/A_t)] \times 100 \quad (4)$$

where A_a = the integrated area of the amorphous-sample diffractogram

A_t = the integrated area of the filament-sample diffractogram

Infrared Analysis

Each variety of silk filaments was analyzed for its basic chemical structure and functional groups using the FTIR spectrometer (model Nicolet Nexus 670) with an ATR (attenuated total reflectance) technique and DTGS detector. The FTIR spectrum of each filament was recorded from 650 to 4000 cm^{-1} with the averaged 100 scans and a resolution of 4 cm^{-1}.

Softening Point

The softening temperature of each sample was determined using the melting apparatus (Sanyo Gallenkamp) by heating the sample and observing it for its softening point.

Burning Test

Silk filaments were tested for their burning behavior according to the AATCC test method 20. They were observed for their appearances near the flame and during burning and for their burning residue.

Strength

Silk tenacity was determined using a Lloyd tensile tester, model L500, according to ASTM D2256. All varieties of silk filament were conditioned overnight before being tested. Each sample of ten inches long was clipped onto the machine and then stretched to breakage with a stretching rate of 300 mm per minute using a 100 N load cell.

Resistance to Sunlight

The silk filaments were tested for their resistance to sunlight by exposing them to imitation sunlight produced by a mercury/tungsten arc lamp in the light fastness tester Shirley (model M237A) for 25 hours, and then testing their tenacity, compared to that before the exposure.

Dyeability

Silk dyeability was determined by first dyeing each silk filament with an Acid Orange 253 at 2% weight of filament (owf), 2% owf of 98% sulfuric acid and 1 g/dm^3 of nonionic wetting agent, in a stainless steel container of the laboratory dyeing machine, Ahiba Polymat, at a liquor ratio of 1:30, at 100 °C for 45 minutes. The dyed filament was removed from the cylinder, air dried and measured for its color strength (K/S before washing) at a wavelength of 520 nanometers using the Macbeth reflectance spectrophotometer (Color-Eye 7000). Then it was washed, dried, and measured for its color strength (K/S after washing). The percentage of dye fixation was calculated by multiplying 100 by the ratio of the K/S after washing over the K/S before washing.

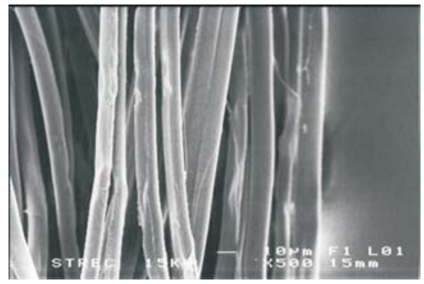
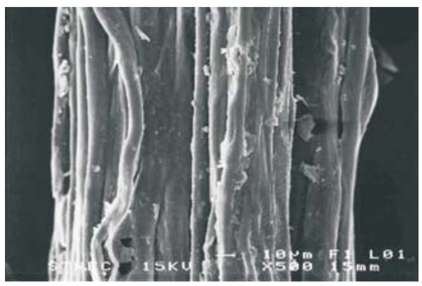
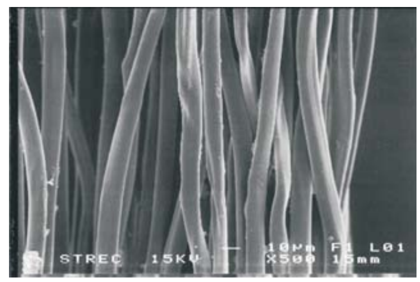
Resistance to Acid, Alkali, and Bleaching Agent

Each variety of silk filament was tested for weight loss after exposure to 2% owf of 98% sulfuric acid in dyeing conditions (see the dyeability section), 2-3 g/dm^3 sodium carbonate in the degumming condition (see the degumming section), and 3 g/dm^3 of 50% hydrogen peroxide in the bleaching condition (pH 10, 95 °C, 45 minutes).

Results and Discussion

Appearance, Cross-Sectional and Longitudinal Views

The silk variety known as Chul 4 was a yellow filament while other varieties of Chul 6, Chul 1 and the imported Chinese silk were white filaments. All filaments were inner layer filaments and they all looked shiny and clean. The SEM micrographs of these filaments showed a similar appearance described as follows. Each piece of raw silk was covered with sericin gluing two filaments together and showed an uneven surface. On the other hand, each degummed silk appeared as an individual filament with triangular cross-sectional shapes and a more even surface. Hand and machine reeled filaments showed a similar appearance under SEM analysis. Figures 1 and 2 show the scanning electron micrographs of the local silk Chul 4 and the imported Chinese silk, reeled by machinery.

Reeling Method	**Longitudinal View**	
	Raw Silk	**Degummed Silk**
Hand		
Machine		

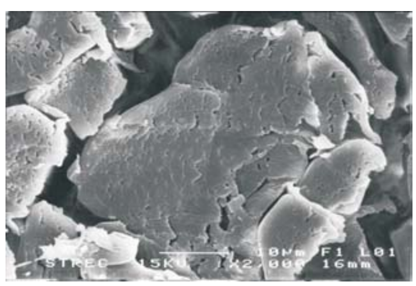
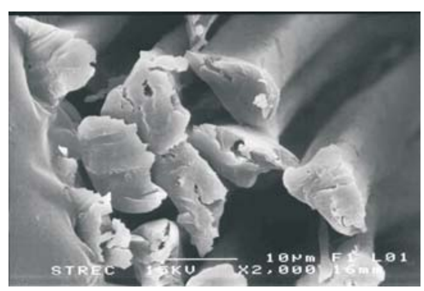
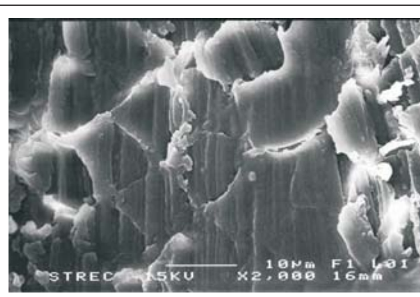
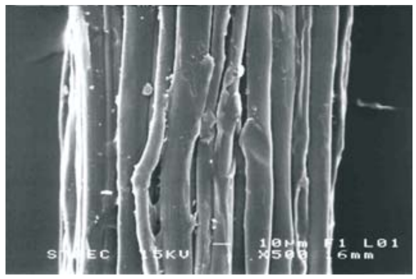
Reeling Method	**Cross Sectional View**	
	Raw Silk	**Degummed Silk**
Hand		
Machine		

Figure 1. Cross sectional and longitudinal views of Chul 4 silk filament under SEM.

Reeling Method	Longitudinal View	
	Raw Silk	**Degummed Silk**
Machine		

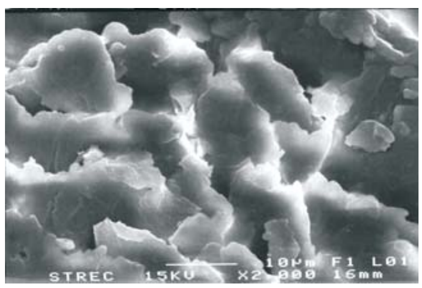
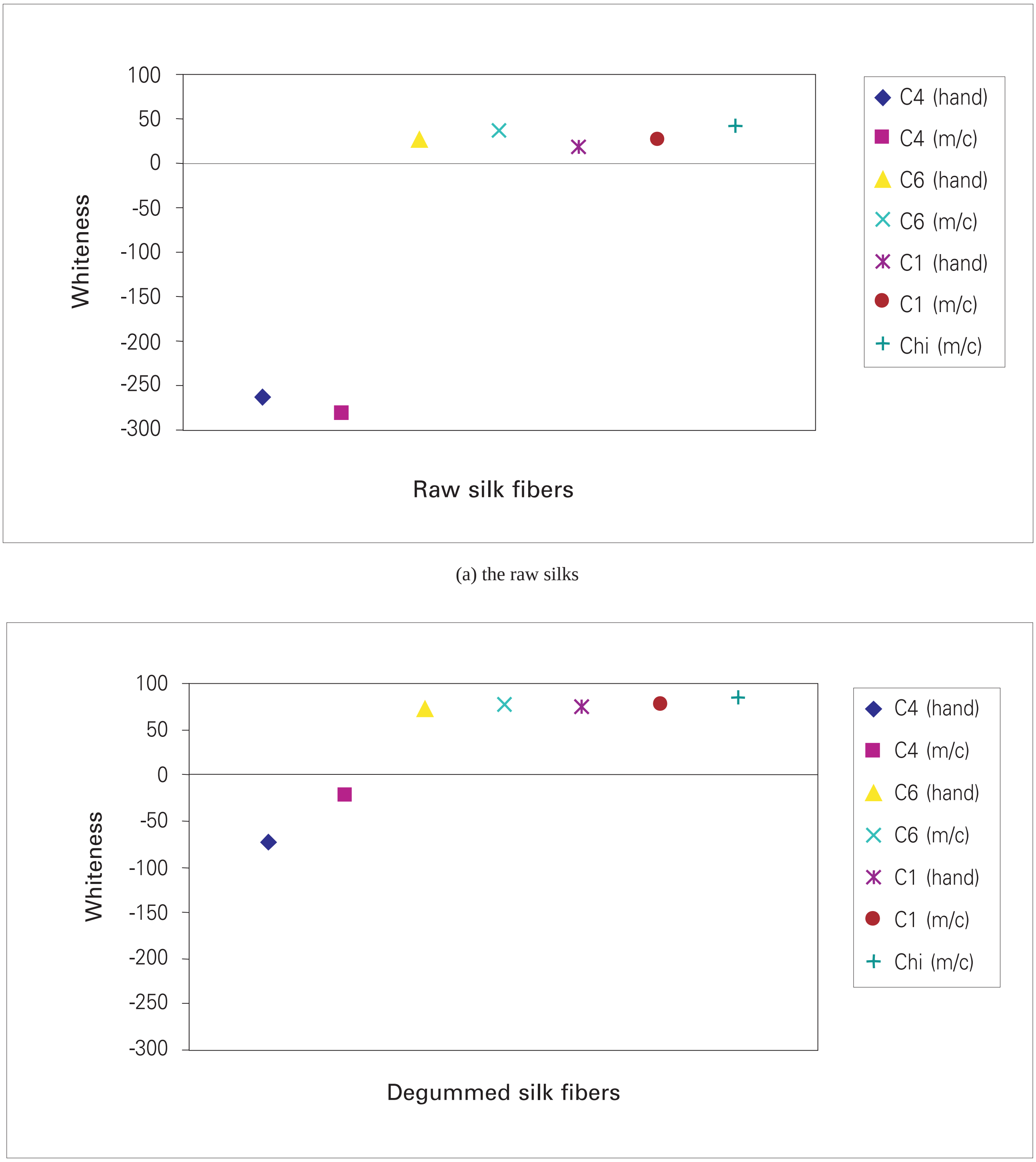
Reeling Method	Cross Sectional View	
	Raw Silk	**Degummed Silk**
Machine		

Figure 2. Cross sectional and longitudinal views of Chinese silk filament under SEM.

Whiteness

The whiteness measurement of the raw and degummed silks shown in Figure 3 indicates the following information. All white filaments had positive values in whiteness while the yellow filament had negative values in whiteness. The imported Chinese silk had the highest whiteness of 42 for the raw filament and 85 for the degummed filament, followed by the local silk Chul 6 and Chul 1 (18-37 for the raw filaments and 72-78 for the degummed filaments). One reason for this result could be that the Chinese silk had a lower number of impurities including sericin on the surface (see degumming loss section) than those on the local silk and thus showed less effect on the whiteness of the Chinese silk. Another reason could be due to the higher whiteness of the Chinese silk fibroin.

Figure 3 also shows that the machine reeled silks had higher whiteness than the hand reeled silks when compared within the same silk variety. The local white silk reeled by machinery had whiteness values of 27 and 37 for the raw filaments (Chul 1 and Chul 6) and 78 for the degummed filaments while those reeled by hand had a lower whiteness value of 18 and 33 for the raw filaments and 74 and 72 for the degummed filaments. This might be due to the different speeds and consistencies of reeling taking place in both reeling methods. The machine reeling could provide a higher reeling speed and better consistency of reeling than the hand reeling, and this could help decrease the number or the thickness of the impurities coated on the filament



(a) the raw silks

(b) the degummed silks

Figure 3. Whiteness of (a) the raw silks and (b) the degummed silks.
[Cl for Chul 1; C4 for Chul 4; C6 for Chul 6; Chi for Chinese filaments; hand for hand reeling; m/c for machine reeling]

surface and improving the filament cleanliness and whiteness.

Not only could the machine reeling improve silk whiteness, degumming also could increase whiteness. All the degummed filaments gave a higher whiteness value than that of the raw filaments in which the degummed Chinese silk had the highest whiteness of 85, followed by the degummed local silks of Chul 6 and Chul 1 (72-78). The degummed yellow silk Chul 4 had less negative values in whiteness than its raw silk. This result indicated that the degumming process could have removed sericin and color substances coated on the filament surface, leaving silks cleaner and whiter.

Denier

Generally the fineness or denier of each silk filament is 1.25 deniers and the double filament gluing together with sericin is in the range of 1.75-4 denier. In this study, it was shown that double filament of the Chinese silk had 2.2 denier for the raw silk and 2.1 denier for the degummed silk while that of the local silks had various degrees of finenesses from 2.2 to 2.5 denier for both the raw and the degummed silks. The only one local white silk reeled by machine, Chul 1, had about the same fineness as the Chinese white silk also reeled by machine. Other local silks were coarser than the Chinese silk. The degummed silks showed the same denier as their raw silks. Differences in fineness among various silk varieties could be due to their different parental genetics, and raising diets and climates, and many other environmental controls. Silk varieties of mixed hybrids among the Thai race and the Japanese or the Chinese race called Chul 4 and Chul 6, respectively, had slightly larger deniers (2.3-2.4 denier) than the silk variety of the mixed hybrid among the Japanese and Chinese races called Chul 1, and the Chinese silk (2.1-2.2 denier) when comparing between the machine reeled silks.

In addition, it was found that the machine reeled filaments (2.2-2.4 denier) had slightly smaller deniers than the hand reeled filaments (2.4-2.5 denier) when compared within the same silk variety and this could be because the high speed of machine reeling controlled the filament drawing ratio and hence reduced the filament size or denier.

Degumming Loss

To remove silk sericin and to improve water and dye absorption of the filaments, degumming is an essential step in silk production. The silk weight loss after the degumming was due to the loss of silk sericin. Generally, silk loses approximately 20% of its weight during degumming. In this research, the silk filaments lost 18.4 -22.4% of their weight after the degumming. The Chinese silk lost the least weight of 18.4% while the local silks lost 19-22.4%. The local silk variety of mixed hybrid between the Japanese and Chinese races Chul 1 lost the highest weight. Differences in the filament weight loss or sericin loss among various silk varieties could be due to the different sericin contents in each filament (different parental genetics, raising diets and climates). In terms of silk reeling methods, it was shown that the machine and hand reeled filaments exhibited approximately the same weight loss or sericin loss upon degumming. The amount of sericin on each silk variety was less affected by the reeling methods but more affected by genetics, raising diets and climate.

Moisture Content

Generally, silk has about 9% of moisture content at 21 °C and 65% RH (relative humidity). In this study, moisture content of the degummed silk filaments was found between 7.9-8.8% while that of the raw silk filaments was 7.4-10.2%. The raw silk filaments are mainly composed of fibroin, covered with sericin substances (amorphous structure) which are capable of moisture absorption. Silk fibroin also contains portions of amorphous and crystalline regions to absorb water and strengthen the filament, respectively. Various silk filaments contain different amounts of sericin and different portions of amorphous and crystalline regions.

Among the silk varieties used in this work, it was found that the

Chinese raw silk filament contained a highest moisture content of 10.2% while the local raw silk filaments contained a lower content of 7.4 -9.6%. The results from the degumming weight loss determination showed that the Chinese silk filament lost the least weight during degumming. In the other word, we could say that the Chinese raw silk filament contained the lowest amount of sericin, but it had the higher moisture content than other raw silk filaments containing the higher sericin content. This could mean that sericin content was not the only factor to influence the moisture absorption of the silk filament. Some other factors such as chain orientation, crystallinity and others could affect the moisture absorption as well.

The effect of the reeling methods on the silk filament's moisture content studied was found that the two local degummed filaments had a similar moisture content for the hand reeled filaments and machine reeled filaments while the one local degummed filament showed a different result. In addition, the local raw silk filament reeled by machine had a lower moisture content than that reeled by hand while the other two raw filaments showed the opposite result. From these outcomes, it was not possible to reach a definite conclusion on how the reeling methods affected the moisture content of silk filaments because of the inconsistent test results from the non-uniformity of the natural fiber.

Relative Density

Silk density determination indicated that the raw silk filaments have a relative density in the range of 1.20-1.26 g/cm^3 and the relative density of the degummed silk filaments was 1.06-1.14 g/cm^3. The degummed filaments showed a lower density than the raw filaments due to the loss of sericin upon degumming. Among all varieties, The Chinese silk filament had the lowest density for both the raw silk filaments and the degummed filaments because the Chinese silk filament had a smaller size (denier), lower weight and lower sericin content than the local silk filaments. Again, it was not possible to find a relationship between the reeling method and silk density due to the same reason as mentioned previously.

Birefringence

The degummed silk filaments were tested for their birefringence in order to study the polymer chain orientation within the filaments. It was found that the local silk filaments reeled by machine had a similar birefringence (0.050-0.053) as that of the machine reeled Chinese silk filament (0.053). The polypeptide chains in these filaments could have a similar degree of orientation. Furthermore, the test results showed that the local filaments reeled by hand had a lower birefringence (0.041-0.047) or a lower degree of polypeptide chain orientation than those reeled by machine (0.050-0.053). It is possible to say that the machine reeling process introduced a higher filament drawing speed and drawing ratio than the hand reeling process and thus it promoted better orientation of polypeptide chains in the machine reeled filaments.

Crystallinity

Generally, silk filament contains 65-70% crystallinity. In this study, the degummed silk filaments were determined for their crystallinity using an X-ray analysis and results are shown in Figure 4. It was found that the local filaments reeled by hand contained 40-68% crystallinity while those reeled by machine contained higher crystallinity of 62-72%. It was also shown earlier that the hand reeled filaments had a lower birefringence than those of machine reeled filaments and thus showed the lower %crystallinity in there. Comparing the local filaments and the Chinese filament both reeled by machine, the test results showed that the local filaments had a higher % crystallinity (62-72%) than the Chinese filament (59%) while the similar birefringence in the range of 0.050-0.053 had been previously reported. All the degummed filaments showed a similar pattern of X-ray diffractograms featuring a broad major peak located at $2\theta = 20.5^{\circ}$ with various peak amplitudes for each silk variety.

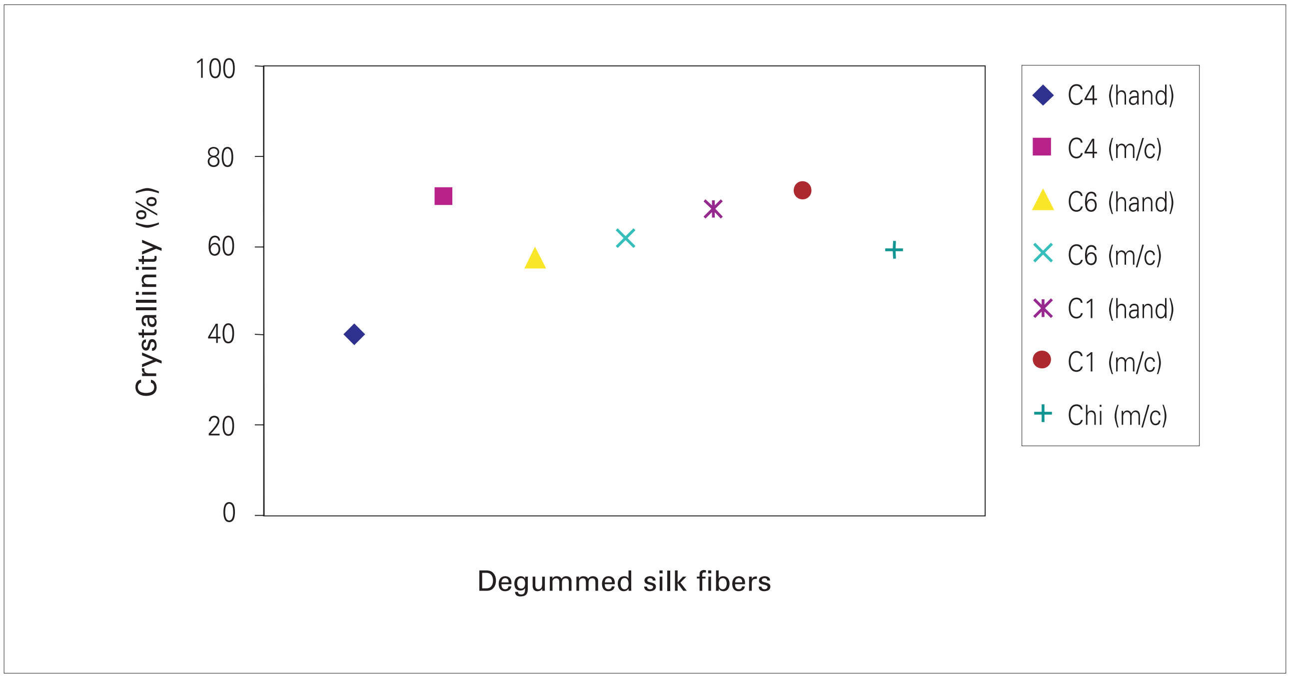


Figure 4. Crystallinity of the degummed silks.
[Cl for local Thai Silk; C4 for Chul 4; C6 for Chul 6; Chi for Chinese filaments; hand for hand reeling; m/c for machine reeling]

Infrared Analysis

All ATR IR spectra of the degummed silk filaments used in this study showed a similar spectral pattern. These spectra indicated that all the silk varieties had the same chemical structure with chemical groups assigned to various peaks as follows. Peak position at 3426-3413 cm^{-1} was assigned to be the N-H stretching, 2966-2920 cm^{-1} was the C-H stretching, 1646-1633 cm^{-1} was the C=O stretching and the N-H stretching (amide I), and 1517-1509 cm^{-1} was the C=O stretching and the N-H stretching (amide II). This result indicated the existence of the amide group (NH-C=O) on polypeptide chains in silk filaments.

Softening Point

Silk does not melt when it is heated. In fact, it begins to yellow at around 100 °C, decomposes at 170 °C, and burns at 420 °C. In this study both the raw and degummed silk filaments were tested for their softening points and it was found that these raw filaments showed softening points ranging from 146 to 160 °C while the degummed filaments showed slightly lower softening points ranging from 145 to 155 °C because the silk sericin covering the raw filaments surface can protect silk fibroin from heat.

For the raw filaments, the results showed that the local filaments reeled by machine rendered softening points in the range of 155-160 °C and that of the Chinese filament possessed a lower temperature at 149 °C due to the lower amount of sericin on the Chinese filament for heat protection (see the degumming loss section). On the other hand, the Chinese degummed filament showed its softening point (153 °C) in the same range of the local degummed filaments (151-155 °C). Silk fibroins of both the Chinese filament and the local filaments could have the same heat resistance.

In terms of reeling techniques, the test results indicated that the local filaments reeled by hand had lower softening points (146-153 °C for the raw filaments and 146-150 °C for the degummed filaments) than those reeled by machinery (155-160 °C for the raw filaments and 151-155 °C for the degummed filaments). The reasons for these results could be due to the higher birefringence and higher crystallinity of the machine reeled filaments (see the birefringence and crystallinity sections).

Burning Test

All the silk filaments showed very similar burning behavior as follows. Both the raw and degummed filaments shrunk on heat when they were placed near a flame. Upon placing them in the flame, they burned immediately. The degummed filaments gave a strong smell similar to hair burning while the raw filaments did not produce a strong smell during burning. After burning the raw filaments, black, grey and hard solid ashes resulted, but while burning the degummed filaments, black and soft ashes developed.

Fiber Strength

The raw and degummed silk filaments were tested for their strength in terms of fiber tenacity in a unit of gram per denier (g/d). The test results indicated that the raw filaments had higher tenacity (2.4-3.6 g/d) than the degummed filaments (1.2-2.5 g/d) due to the presence of sericin. Sericin on the raw filaments could help in increasing the fiber strength or tenacity resulting from its elastic amorphous structure. The Chinese raw filaments and the degummed filaments had approximately the same fiber tenacity (2.5 g/d for the raw filament and 2.4 g/d for the degummed filament). In the other words, the Chinese silk filament could maintain its strength after degumming (only 4% loss) while the local silk filaments lost 20-58% of fiber tenacity after degumming because the degumming agents introduced more fiber damage to the local filaments than to the Chinese filament.

In terms of reeling methods, it was found that the local raw filaments reeled by machine had a slightly lower tenacity (2.4 -3.1 g/d) than those reeled by hand (2.6-3.6 g/d) while the local degummed filaments showed the inconsistent tenacity of the machine and hand reeled filaments. The previous test results on birefringence, crystallinity and the softening point of the local raw and local degummed filaments indicated that the filaments reeled by machine had a higher birefringence, crystallinity and softening point than those reeled by hand. Thus it should be expected that the former filaments have a higher tenacity than the latter; unfortunately this was not the case. This is caused by the unevenness of the natural silk fiber from silk genetics and raising condition of the silk worms.

Resistance to Sunlight

Generally, silk fiber cannot resist sunlight because it tends to absorb UV radiation from sunlight through the peptide bonds and a small amount of the disulfide bonds on polypeptide chains and their natural pigments within the fiber. The high energy of UV radiation can later break these covalent bonds, degrade the fiber and decrease the fiber strength.

This study revealed that after a 25-hour exposure to the imitation sunlight, both the raw and degummed silk filaments showed a significant strength loss in terms of %tenacity loss (38-53% for the raw filaments and 44-54% for the degummed filaments). The raw filaments lost less strength than their degummed filaments because the sericin on the raw filaments helped protect the silk from UV destruction. It was also found that the Chinese raw filament showed the lowest tenacity loss (38% loss) while its degummed filament showed the highest tenacity loss (54% loss) after a sunlight exposure of 25 hours, compared with the local raw and local degummed filaments. The Chinese degummed filament or silk fibroin could be damaged more by sunlight or have less resistance to the sunlight than the local silk fibroin. On the other hand, the test results showed that the local raw filaments lost 50-53% and their degummed filaments lost 44-50% after the exposure.

Silk resistance to sunlight can be influenced by the parental genetic of each silk variety including many factors such as the number of peptide bonds and the various amino acid contents on polypeptide chains, natural pigment content within silk fibroin and silk sericin, sericin content, etc. It has been shown previously that the Chinese degummed filament has a higher loss of tenacity than its raw filament after sunlight exposure. This could be explained by the fact that the resistance to sunlight of the Chinese filament is influenced more by the sericin content than by other factors. For the local filaments, most of the raw filaments and degummed filaments showed a similar loss of tenacity and thus the sericin on filaments might not play a significant role in protecting the local silks from sunlight. Instead, the silk fibroin of the local filaments (amino acids, natural pigments) could play a major role.

In terms of reeling techniques, it was shown that most of the local silks reeled by hand and by machine had similar tenacity loss after the exposure. There might not be a relationship between the reeling method and the resistance to sunlight of the silk filaments.

Dyeability

The degummed silk filaments were dyed with acid dye orange 253 and they were measured for %dye fixation. The results in Figure 5 indicated that these filaments showed %dye fixation in the range of 72-85%. The Chinese filament had the lowest dye fixation of 72% while the local filaments had a higher fixation of 74-83%. In this study, the dye fixation was calculated from the measurement of silk color strength (K/S) before and after washing (see the dyeability section) using a colorimetric method. This method showed the color strength of the silk surface, not within the silk filament. Therefore, the silk filament with a higher surface area or smaller size (denier) would show lower color strength than the silk filament with a lower surface area or larger size (denier) when they were dyed at the same dye concentration because the smaller silk needs a higher amount of dye or needs to be dyed at a higher dye concentration in order to obtain the same color strength as the larger silk. This could be the reason that the smaller denier of the Chinese silk filament reeled by machine (see denier section) showed a lower dye fixation than

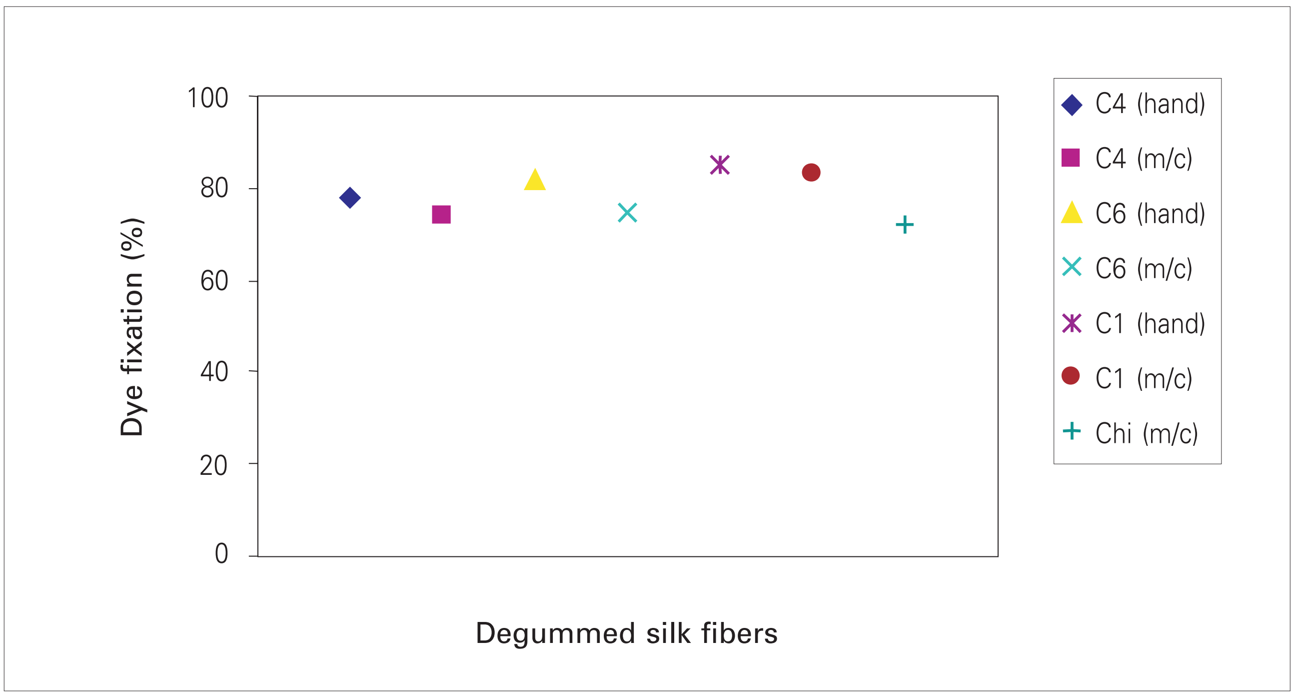


Figure 5. Dye fixations of the degummed silks.
[Cl for local Thai Silk; C4 for Chul 4; C6 for Chul 6; Chi for Chinese filaments; hand for hand reeling; m/c for machine reeling]

a larger denier of the local silk filaments reeled by machine when they were dyed at the same dye concentration. The internal properties of silk such as birefringence, crystallinity, moisture content, etc. might not play significant roles in this case. The surface chemistry of the typical functional groups of silk fiber and the acidic dye can be a major attribute to the different color strength. The amount of all amino acid types, i.e., the non-polar amino acid, acid amino acid, basic amino acid and sulfur-complex amino acid, can interact with the acid dye via an acid-base interaction to give different color strength. We anticipate that a certain type of amino acid, for example glycine, in the sericin of the silk can be used a padding agent to enhance color reception and thus higher color strength. This research is now underway.

In addition, the reeling method in relation to the denier could be another important contributor to color strength. According to the reeling methods, it was shown that machine reeled filaments had a slightly lower dye fixation (74 - 83%) than hand reeled filaments (78-85%). The machine reeled filaments had a lower denier than the hand reeled filaments (see the denier section) and thus it had a smaller surface area to accept dye and thus showed a lower dye fixation measuring by the colorimetric method.

Resistance to Acid, Alkali, and Bleaching Agent

The raw and degummed silk filaments were tested for acid resistance by immersing in a solution of sulfuric acid in dyeing condition. After this acid exposure, a very low loss of the silk weight of 1-1.5% for the raw silk and 0.5-0.7% for the degummed silk was shown. This small weight loss could come from the loss of some water soluble materials rather than from the loss from the sericin and silk fiber because sericin and fibroin proteins should have more resistance to acid than to alkali. The test results in this study indicated that all the silk varieties showed a high resistance to acid. There was an insignificant difference in the weight loss of the silk after the acid exposure between the silk reeled by hand and those reeled by machine, and between the Chinese silk and the local silk.

Generally, silk fiber or fibroin can be damaged when exposed to alkali condition such as degumming due to their vulnerable peptide bonds to alkali. In this study, the raw and degummed filaments were exposed to sodium carbonate under a degumming condition and then were tested for weight loss. It was shown that the raw filaments lost 15.7-27% weight while the degummed filaments lost only 11-14.4% weight after an alkaline exposure. This weight loss came mainly from the loss of sericin, and partly from the loss of fiber and/or water soluble substances. The Chinese raw silk lost the lowest weight of 15.7% while its degummed silk lost the greatest weight of 14.4% for this study, compared with the local raw silk of 23.1-27%, and the local degummed silk of only 11-13.8%. Because among all the silk varieties, the Chinese raw silk contained the lowest content of sericin (see the degumming loss section) and thus it lost the lowest weight after the exposure. On the other hand, the silk fibroin of the degummed Chinese silk was damaged more by the alkaline solution than the silk fibroin of the degummed local silks. All the silk varieties in this study showed very low resistance to alkali. The silks reeled by hand and those reeled by machine showed an insignificant difference in the weight loss after the exposure. In other words, the silk reeling methods had no influence on the silk resistance to alkali.

In general, silk bleaching with an oxidizing agent of hydrogen peroxide is conducted at an alkali condition and silk can be damaged by these chemicals (hydrogen peroxide and sodium carbonate). The oxidizing agent can oxidize the polypeptide chain in fibers, and degrade it as well as decrease the fiber strength. This leads to the loss of fiber but in a smaller degree when compared to the damage from the alkali degumming. In this study, it was shown that the raw filaments lost 7.4-9.8% weight and the degummed filaments lost 2.1-3.2% weight after bleaching. The Chinese raw silk filaments and the degummed filaments lost the highest weight of 9.8% and 3.2%, respectively, compared with the loss of the local raw silk filaments (7.4-8%) and the degummed filaments (2.1-2.4%). The Chinese silk had a lower resistance to bleaching condition than the local silk. Again, there was no correlation between the reeling methods and the silk resistance to bleaching found in this study.

All the silk fibers used in this study showed the same behavior as they were highly vulnerable to alkali, less to bleaching with an advantage of a great resistance to acid. In addition, no clear correlation was found between the reeling methods (by hand and by machine) and the silk resistance to acid, alkali and the bleaching agent.

Possible Applications for Silk Fabric Production, Dyeing and Printing

The characterized data obtained by this work conform to the fundamental theory for silk testing properties. It is the first time that such a comparison of silk properties reeled by hand and machine is performed. More characterization will be carried out for a complete data base for applications in silk industry. Based on this type of data, appropriate fiber properties from the reeling techniques can be adjusted or modified to suit its particular requirement in production of silk fiber. Additionally, a proper fiber selection in correlation with fabric and its color appearance, fabric and printed fabric permanence based on color properties of the outer and inner layer fibers, and performance and usability of fabric itself and printed fabrics based on denier, crystallinity, and relative density can be achieved. New fabric designs can be created upon weaving the outer-layer silk yarns having darker colors in combination with the inner layer silk yarns containing lighter colors to resulting in a new unique, aesthetic appearance of stylist Thai silk clothing. Fiber characteristics such as homogeneity, denier, and liquid absorption of the fiber as the major influencing factors for fidelity, resolution, and dot gain of printed fabrics can be manipulated. Information on resistance to sunlight, bleaching agent and acid-base conditions can be a guideline for formulations of dyeing chemistry, printing ink chemistry and detergent chemistry using high performance colorants to reduce damages upon exposure to these environments.

Conclusions

In this study, three Thai silk filaments reeled by hand and by machine were analyzed compara tively for various properties. It was found that the reeling method could affect significantly the silk properties such as whiteness, polypeptide chain orientation or birefringence, crystallinity, heat resistance or softening point, dyeability, and denier or fiber size. The machine reeling increased the silk whiteness, birefringence, crystallinity, and softening point while decreasing the silk denier and dyeability in comparison with the hand reeling.

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บทคัดย่อ **สมบัติของไหมไทยเชิงอุตสาหกรรมสาวด้วยมือและเครื่องจักร**

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งานวิจัยนี้ได้ศึกษาสมบัติของเส้นใยจากหนอนไหม ๓ ชนิด ที่ผลิตในประเทศไทย และเส้นใยไหม ๑ ชนิด ที่นำเข้าจากต่างประเทศ เปรียบเทียบสมบัติของเส้นใยไหมเหล่านี้ที่สาวด้วยมือและสาวด้วยเครื่องจักร ซึ่งทดสอบตามมาตรฐานสากลคือ ความขาวและความเหลือง ขนาดเส้นใยไหม (ดีเนียร์) น้ำหนักที่หายไปจากการลอกกาวไหม ปริมาณความชื้น ความหนาแน่นสัมพัทธ์ การจัดเรียงตัวของโซ่พอลิเมอร์ในเส้นใยไหม (birefringence) ปริมาณผลึก องค์ประกอบทางเคมี จุดอ่อนตัว พฤติกรรมการเผาไหม้ ความเหนียวหนืด (tenacity) ความทนแสงแดด การตรึงสีย้อม ความทนกรด ด่าง และภาวะฟอกขาว จากการศึกษาได้พบว่า เส้นไหมสาวด้วยมือให้ค่าความขาว การเรียงตัวของโซ่พอลิเมอร์ ปริมาณผลึก และจุดอ่อนตัวต่ำกว่าเส้นไหมสาวด้วยเครื่องจักร ในทางตรงข้าม เส้นใยสาวด้วยมือให้ค่าขนาดเส้นใยและการตรึงสีย้อมดีกว่า เส้นใยไหมในประเทศมีค่าขนาดเส้นใย น้ำหนักที่หายไปจากการลอกกาวไหม ความหนาแน่นสัมพัทธ์ ปริมาณผลึก การตรึงสีย้อม และการทนด่างและสารฟอกขาวได้ดีกว่าเส้นไหมนำเข้าจากประเทศจีน.

คำสำคัญ **: ไหมไทย, สาวด้วยมือ, สาวด้วยเครื่อง, สมบัติต่าง ๆ**