Silk : Queen of Fibres - The Concise Story

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1. Introduction

Most historians agree that silk and sericulture -- the cultivation of silkworms -- had their origin in China nearly 2500 BC when the Empress Si-Ling-Chi, a queen of the famous Emperor Huang-Ti, learned how to rear the silkworms and unwind their cocoons to produce fine filament fibres. After finding this knowledge, China kept it as a secret and held a monopoly in the silk industry for nearly 4,000 years. After this period, sericulture spread to Korea and Japan [1,2] and it also spread around the world. Details about silk history and sericulture can be found in references 3 to 7.

Silk, called the '*Queen of fibres*', is a continuous protein fibre produced by the silkworm so as to form its cocoon [8]. The silk fibre is also produced by some spiders belonging to the Arachnida family [1,9,10]. Unlike the silkworms' fibre, the spiders' fibre cannot be commercially produced, and therefore, the silk fibre referred to in this work is the fibre coming from the silkworm.

The silk fibre is a natural animal fibre. Unlike wool, silk contains a very small amount of a sulphur [11]. There are two main types of the silkworms: mulberry silk (Bombyx mori), also called 'cultivated silk', and 'wild silk' of which Tussah silk is the most important representative. Mulberry silk is produced by silkworm larvae cultivated in provided habitats and fed with fleshy picked mulberry leaves. Cultivated silk is different from Tussah silk--native

to China and India--in that Tussah silk is fed almost only on oak leaves. Cultivated silks are fine, almost white (when degummed) and soft filaments with lustre. Nearly 80-85 % of the world silk production consists of cultivated silks. While wild silks are coarser, more irregular and brownish in appearance, they are never as white as the cultivated silk filament [12].

Thai silk is one of the mulberry silkworm (*Bombyx mori*) silks but it differs somewhat in the appearance. It is yellower in colour, the filaments are coarser, and it has more silk gum (e.g. up to 38 %) than normal mulberry silk (e.g. 20-25 %) [11,13]. These characteristics cause Thai silk to have its own style after weaving. Thai silk products are mainly produced by domestic industries in the northern and north-eastern parts of Thailand. Nowadays, the most famous Thai silk products are handicraft and neck-tie. FAO reports on sericulture indicate that the 1997 world production of raw silk was 86,704 tonnes, valued at over US$1.6 billion [14].

2. Mulberry silkworms

Mulberry silkworms can be divided into three groups: [15]

1. **Univoltine** (one generation per year)

Univoltine breed is usually found in Europe. Because of the cold climate, the eggs are dormant in winter and they are hatched only in spring. Therefore, they generate the silkworms once a year.

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2. Bivoltine (two generations per year)

Bivoltine breed is normally found in Japan, Chain and Korea. The life cycle of the breed starts twice within the same year because the climate is suitable for developing two life cycles per year.

3. Polyvoltine (up to eight generations per year)

Polyvoltine breed is customarily found in tropical zone. After eggs are laid by female butterflies, the eggs will be hatched after between nine and twelve days.

The major groups of silkworms are univoltine and bivoltine breeds.

The hybrid silkworm is a cross between two or more pure breeds. The progeny will be a new breed of silkworm combining the good characteristics of the parents and generating a strong silkworm because of the hybrid vigour. The hybrid silkworm tends to grow up very fast and gives better filament quality than its parents.

In entomology, silk is grouped in the phylum Arthropoda which has a complete metamorphosis. Entomological classification of mulberry silkworm is: [16,17]

Phylum   Arthropoda
Class   Hexapoda or Insecta
Sub-class   Pterygota
Division   Endopterygota
Order   Lepidoptera
Family   Bombycidae
Genus   Bombyx
Species   mori

Generally, Bombyx mori is represented an entomological classification of mulberry silkworms.

3. Life cycle of the silkworm

Metamorphosis of silkworm has four stages as follows:[18]

1. Stage I (eggs), which develop into caterpillars or silkworms.

2. Stage II (larvae), which spin the filament fibre to make their cocoons for protection and metamorphosis into the pupae.

3. Stage III (pupae), which emerge from the cocoons as moths (butterflies).

4. Stage IV (moths), of which the male and female moths breed and the female moth lays eggs and the eggs will continue the next life cycle (Figure 1.1).
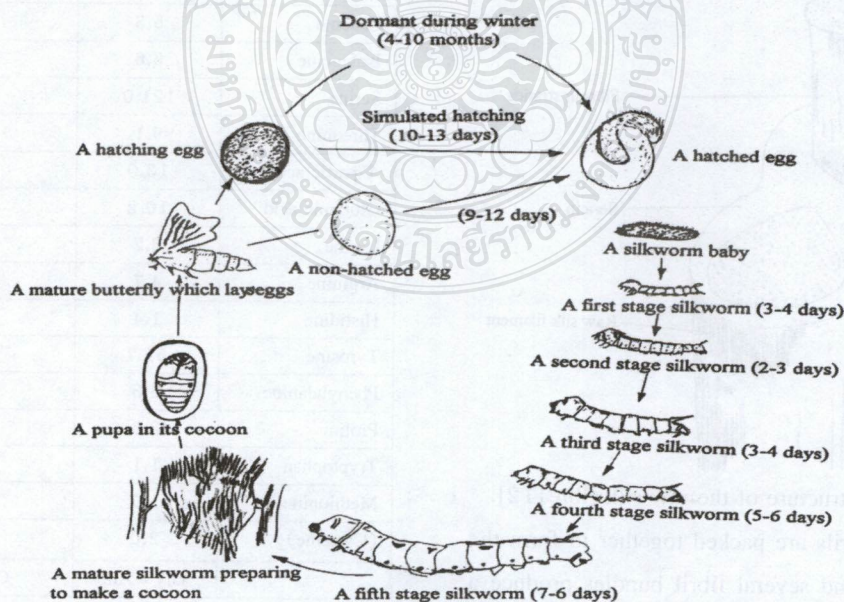

Figure 1.1 Life cycle of silkworm [18].

4. Structure of the silk fibre

The spinning process of the silkworm has been described [9,19,20]. The mature silkworm builds its cocoon by extruding a viscous fluid from two large glands in the body of the silkworm. This solution is extruded through two ducts in the head of the silkworm into a common spinneret. The viscous part (fibroin) is covered by another secretion (sericin) which flows from two other symmetrically placed glands. These two components are cemented together by emerging into the air, coagulating and producing a firm continuous filament.

As a consequence of this spinning process, the fibre has two main parts called **sericin and fibroin**. Sericin, called silk gum, is a minor component of the fibre (i.e. 25 % of the weight of

raw silk) and it also has some impurities such as waxes, fats and pigments. Sericin is a yellow, brittle and inelastic substance. It acts as an adhesive for the twin fibroin filaments and conceals the unique lustre of fibroin. Sericin is known as an amorphous structure and it is dissolved in a hot soap solution. Komatsu [9,13] claimed that sericin may be separated into sericin I, II, III, and IV by using their different solubilities in hot water and assessing the degree of solubility by UV adsorption. The greatest sericin content is present in the outer layer of a cocoon whereas the least sericin proportion is present in the innermost layer of a cocoon.

Fibroin is the principal water insoluble protein (i.e. 78 % of the weight of raw silk). Fibroin has a highly oriented and crystalline structure.
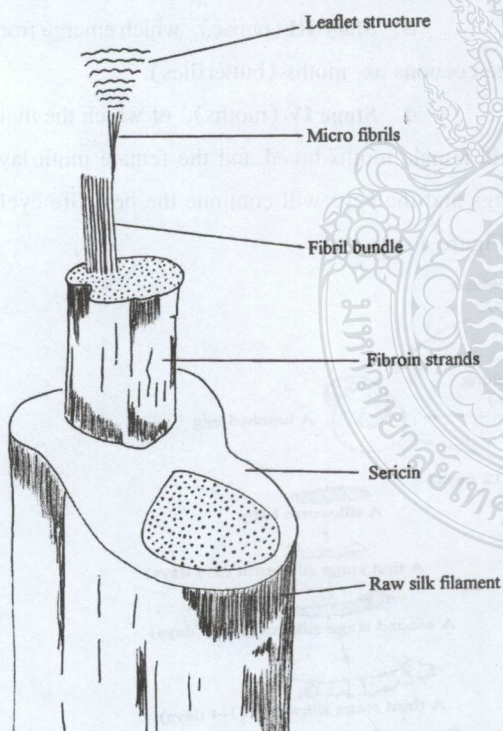
Figure 1.2 Structure of the raw silk fibre [12].

Microfibrils are packed together to form the fibril bundle and several fibril bundles produce a single strand.

Table 1.1 Amino acid compositions of silk fibroins (residues/1000 residues) [9].

Amino acids	B.mori fibre	Tussah A. pernyi fibre
Glycine	446.0	265.0
Alanine	294.0	441.0
Valine	22.0	7.0
Leucine	5.3	8.0
Isoleucine	6.6	–
Serine	121.0	118.0
Threonine	9.1	1.0
Aspartic acid	13.0	47.0
Glutamic acid	10.2	8.0
Lysine	3.2	1.0
Arginine	4.7	26.0
Histidine	1.4	8.0
Tyrosine	51.7	49.0
Phenylalanine	6.3	6.0
Proline	3.6	3.0
Tryptophan	1.1	11.0
Methionine	1.0	–
(Cysteine)$_2$	2.0	–
	Gly > Ala	Gly < Ala

Table 1.2 Amino acid compositions of silk sericins (residues/1000 residues) [9].

Amino acids	B.mori cocoon	Tussah A. pernyi cocoon
Glycine	127.0	149.9
Alanine	55.1	27.8
Valine	26.8	11.9
Leucine	7.2	9.9
Isoleucine	5.5	8.0
Serine	**319.7**	**226.3**
Threonine	82.5	149.6
Aspartic acid	138.4	122.5
Glutamic acid	58.0	67.4
Lysine	32.6	14.7
Arginine	28.6	54.5
Histidine	13.0	25.0
Tyrosine	34.0	49.2
Phenylalanine	4.3	6.0
Proline	5.7	19.1
Tryptophan	-	-
Methionine	0.5	1.3
(Cysteine)$_2$	1.4	1.8

Tables 1.1 and 1.2 show that there are different proportions of amino acid residues in fibroin and sericin. Fibroin has high proportions of alanine, glycine and serine. A small amount of cysteine residues gives a very small amount of sulphur in the fibre. Fibroin contains only a small amount of amino acids which have acid side chains. The amount of basic side groups in fibroin is relatively low. Because of this, the amounts of acid and alkali that can be absorbed by silk are relatively lower than those absorbed by wool (ca. 0.2 equivalent per kg of silk). The isoelectric point of silk fibre is around pH 5. There is a low proportion of amino acid residues with large side chains in silk. Hydrogen bonding is important in fibroin. X-ray structural analyses of the crystalline domains of fibroin show that the peptide chains pack in fully extended forms.
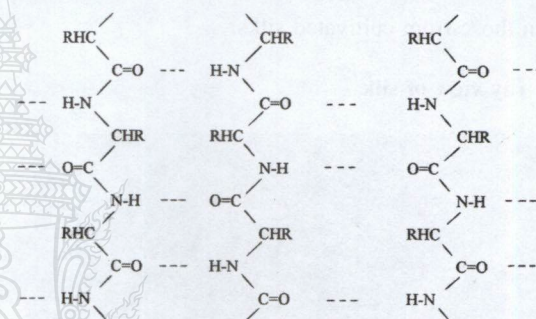

Figure 1.3 Crystalline structure of the polypeptide chains in silk fibroin [12]. (where ____ represents hydrogen bonding)

5. Physical properties of silk

Microscopy of the silk fibre

Figure 1.4 shows that the cross-section of raw silk is roughly elliptical. It shows the triangular twin fibroin filaments, completely covered by sericin, which normally face each other.
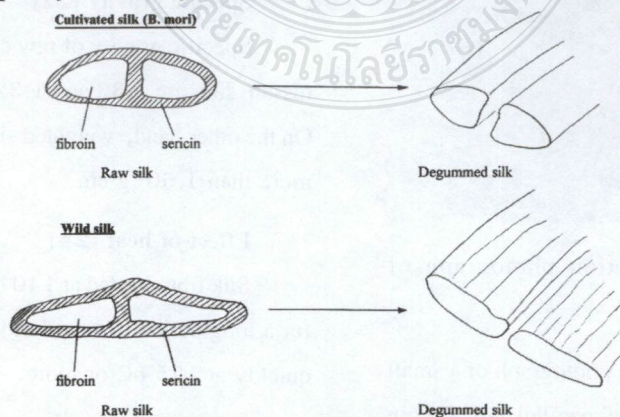

Figure 1.4 Cross section, longitudinal view and perspective of silk filaments [12].

After the degumming process, the two triangular fibroin filaments (brins) separate into individual filaments giving different fibre geometry from the raw silk (i.e. a finer fibre and a more lustrous fibre).

Shape and appearance

Silk filaments are approximately 900 – 1700 metres long. The diameter of the silk filament is from 9 to 11 microns. A raw cultivated silk is off-white to yellow in colour. Unlike cultivated silks, wild silks are uneven, brown and slightly less lustrous than those from cultivated silks.
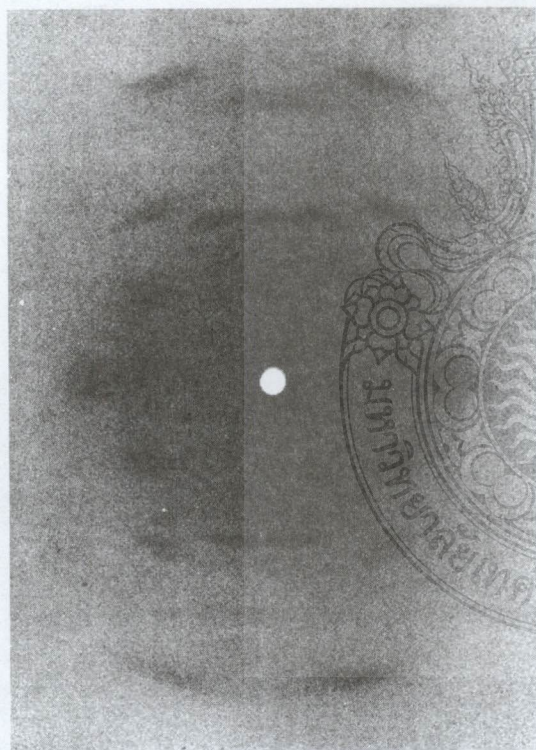
X- ray view of silk

Figure 1.5 X-ray diffraction photograph of fibroin [21].

This figure is an X-ray photograph of a small bundle about 1 mm thick of parallel silk fibroin fibres. It shows that fibroin consists of non-crystalline and crystalline regions. The crystalline region tends to be oriented along the fibre axis because the fibre is drawn as it is extruded from the spinnerets of the silkworm.

Hygroscopic nature

The conventional moisture region of silk is about 11.0 % compared with the mercerised cotton fibre which has conventional moisture regain 10.5 % [22]. The amount of moisture absorbed by silk is dependent on its previous history such as whether it is raw or degummed silk, on the species of silk as well as on the atmospheric humidity.

Tensile properties

Silk fibre is extremely strong. A filament of silk is stronger than an equal diameter filament of steel [3]. Normally, the dry silk fibre has a tenacity varying from 2.4 to 5.1 grams per denier. The wet strength of the fibre is about 80-85 % of the dry strength [23].

Elongation [24]

Elongation at break of silk filaments is around 20-25 % under normal conditions. The extension at break is 33 % at 100 % RH.

Specific gravity [22]

Specific gravity of raw cultivated silk and raw tussah silk are 1.33 and 1.32 g cm^{-3} respectively. On the other hand, weighted silk has specific gravity more than 1.60 g cm^{-3}.

Effect of heat [24]

Silk fibre heated at 140 oC remains unaffected for a long period of time but it is decomposed very quickly at 175 oC or more.

Effect of UV radiation

Tsukada and Hirabayashi [25] found that the strength and elongation of silk fibroin fibres were decreased when the fibres were exposed to the UV radiation. The degree of the crystallinity was not affected by the radiation treatment.

6. Chemical properties

Effect of water

Silk is not dissolved by water at room temperature but silk may lose weight in boiling water or steam at $100^{\circ}C$ [26].

Effect of acids and alkalis [26,27]

Acids and alkalis cause hydrolysis of the polypeptide chains in the fibre. It has been claimed that pH values between 4 and 8 cause the least damage to the fibre [26]. Acid hydrolysis tends to be more damaging to fibre than alkaline hydrolysis.

Acid hydrolysis occurs at nearly all the peptide linkages in the chain while alkali hydrolysis firstly attacks at the end of the peptide chains. Concentrated sulphuric acid and hydrochloric acid will dissolve the fibre; nitric acid colours silk yellow. Dilute acids do not attack the fibre under mild conditions.

Strong hot caustic alkalis will readily dissolve the fibre. Weak alkalis such as soap, borax and ammonia normally dissolve sericin but they also attack fibroin when the treatment time at boiling point is prolonged.

Effect of organic solvents [24]

The commonly used dry cleaning solvents do not dissolve the fibre.

Effect of oxidising agents [26,28]

Oxidation reactions are very complex and are considered to take place at the side chains of tyrosine, the amino terminal residues of the main chains and at the peptide bonds. Fibroin is highly vulnerable to oxidising agents. Therefore, care must be taken when bleaching the fibre.

Hydrogen peroxide and some peracids are normally used in the bleaching process of raw silk. It has been found that peracetic acid causes a more destructive effect with fibroin than hydrogen peroxide does.

Effect of reducing agents [26,28]

It is known that fibroin resists the reducing agents such as hydrosulphite, sulphurous acid and its salts.

7. Silk production [29-31]

One of the first operations in silk production is a reeling process [30]. Before being reeled, the cocoons must be sorted carefully for size, quality and defects. The cocoons are immersed into a hot water bath, which softens the sericin holding the filaments together. The pupae in fresh cocoons are killed at this stage. The filament ends can be found on the surface of cocoons, unwound and twisted from several cocoons (e.g. seven to eight cocoons) in order to make a raw silk multi filament yarn between 20 and 25 denier (the weight in g of 9000 m). Moreover, this process also gets rid of a certain small amount of sericin in the fibre.

Frequently, the filaments are accumulated further by a process called as throwing, the process of producing twisted silk yarn from reeled silk [32]. Hence it produces 'thrown silk' which is a suitable twisted yarn for producing a specific fabric by knitting or weaving.

8. Degumming silk

Derived from French *word Degommage* [33], degumming is at the heart of wet processing of raw silk due to the fact that the raw silk contains the two components fibroin, and sericin which covers

the filaments. Sericin contains some impurities, for example, waxes, fats, mineral salts and pigments. Sericin has the same amino acid residues as fibroin but the proportions contained in both components are quite different. As a result of this, the degumming process must be carefully carried out on silk in the appropriate conditions otherwise the fibroin may be damaged. The pH range from 4 to 8 is normally safe for fibroin [34]. It has been found that alkaline conditions are less harmful to fibroin than acid conditions [34]. In contrast to fibroin, the solubility of sericin is very high at pH values between 1.5 and 2 and between 9.5 and 10.5 (Figure 1.6).
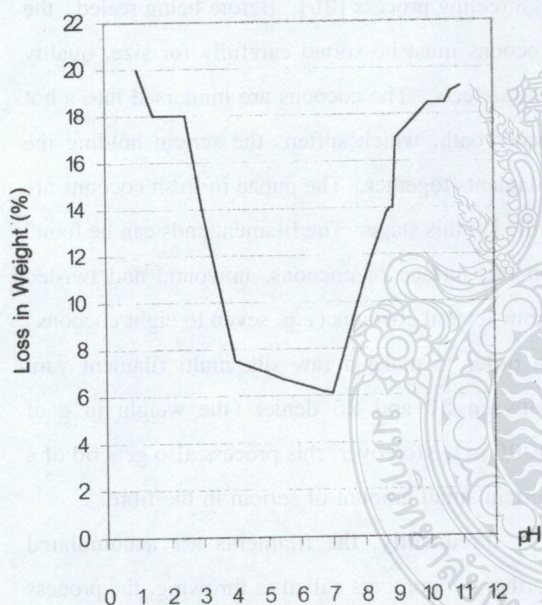

Figure 1.6 Effect of pH of the medium on removal of sericin (in percentage weight loss compared with undegummed weight of fibre [34,35]. (The time, temperature and solution composition are not given in refs. 34 and 35).

The main purposes of the degumming process are to remove the sericin from the fibre, to remove some impurities (e.g. waxes, fats, mineral salts)

affecting both the dyeing and printing processes, to make the fibre highly absorbent for dyes and chemicals, and to reveal the lustre of fibroin and to improve the appearance of the fibre [36]. The sericin is removed from the fibre but the fibroin must not be damaged at the same time.

The degumming processes are classified into five methods as follows:

8.1 Degumming with water under pressure at 115°C

As mentioned before, water at room tempera ture does not dissolve silk but silk is highly suscep tible to dissolution in boiling water. For this reason, this process gives a risk of the fibroin being damaged when the time of treatment is prolonged. This process needs large autoclaves to treat the fibre in the silk industry. A further disadvantage is that this process gives incomplete degumming and sometimes soap or synthetic detergent must be added to improve the degumming effect. Therefore, this process is very difficult to control and now it is not used in the silk industry [37].

8.2 Degumming with soap (ca. 98°C)

Marseilles soap, an olive oil soap, is an outstanding soap for degumming [38]. For example, this process may be carried out using 10-20 g/l soap at 92-98°C for 2-4 hours adjusted pH to 10.2-10.5 in order to react effectively upon the sericin [39,40]. As a result of the high temperature, this process tends to attack both sericin and fibroin because of the sensitive nature of fibroin itself and the chemical similarity of fibroin and sericin [41]. Moreover, the most important requirement of the process is a soft water to avoid the formation of a calcium soap.

8.3. Degumming with synthetic detergent (ca. 98°C)

Synthetic detergents play a crucial role in this process because they have some advantages over soap such as reducing the time of treatment (e.g. 30-40 min at 98°C) and damaging the fibre less [42,43].

Shukla [44] suggested that non-ionic synthetic detergent aided the removal of sericin without affecting the tensile strength of the fibre. He also claimed that the degumming process using 2.5 g/l non-ionic synthetic detergent at pH 11.5 for 30 minutes gave a most efficient degumming effect.

The problem of this process is that it is carried out at high temperature (e.g. at 98°C) and high pH (e.g. at pH 11.5). Therefore, the temperature, the time of treatment and the amount of detergent used must be properly controlled to avoid damage to the fibroin [45].

8.4 Degumming with acid (ca. 98 oC) [46–48]

Some acids such as sulphuric, hydrochloric, tartaric and citric acids can be used as degumming agents. This process has not received much attention in the silk industry because of the idea that degumming in alkaline solution is safer for fibroin than in acid solution. It has been found that the complete degumming of silk with strong mineral acids (e.g.

sulphuric and hydrochloric acids) cannot be achieved without harm to the fibroin.

8.5 Degumming with enzymes

Enzymes are proteins, catalysing a specific chemical reaction, which are known as 'bio-catalysts'. Generally, enzymes appear in living cells. Therefore, they work at atmospheric pressure and in mild conditions (e.g. at 40°C, pH 8.0). Different enzymes may cause hydrolysis, reduction, oxidation, coagulation and decomposition reactions. Hydrolytic enzymes are commonly used in the textile industry: e.g. cellulase [49], trypsin and papain [37].

Some properties of enzymes are as follows [50]:

1. enzymes are complex and high molecular weight protein molecules,

2. enzymes are susceptible to high temperatures and pH values outside their optimum ranges because they can be denatured,

3. enzymes react at specific parts of the substrate molecule depending on their active sites and types, and

4. enzyme reactions are reversible reactions.

$$\text{e.g.} \quad A + B \rightleftharpoons C$$
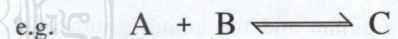
Enzyme reactions

The 'Lock-key theory' simply explains enzyme reactions (Figure 1.7) [50,51].

1. Enzyme.
2. Substrate molecule.
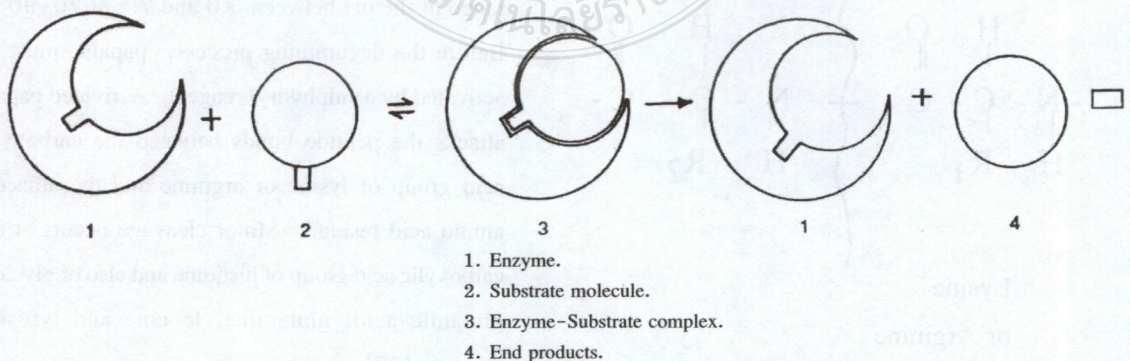3. Enzyme-Substrate complex.
4. End products.

Figure 1.7 Nature of an enzyme reaction [50].

In order to react with substrate as a catalyst, enzyme has an active site and the substrate molecule fits the active site like a key fitting into a lock forming an enzyme-substrate complex. The enzyme-substrate complex then releases an end product and a regenerated enzyme molecule. The regenerated enzyme will then generate a new cycle.
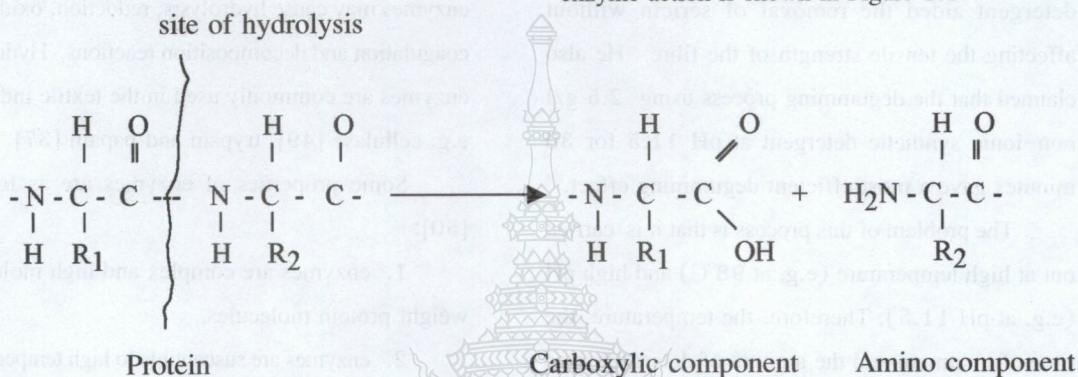
site of hydrolysis

Protein

Figure 1.8 Proteolytic enzyme action on protein [50].

Trypsin

Secreted from the pancreas, trypsin is a serine protease which is most active in the pH range between 7 and 9 at 37°C. It reacts with peptide bonds between the carboxylic acid group of lysine or arginine and the amino group of the adjacent amino acid residue [37].
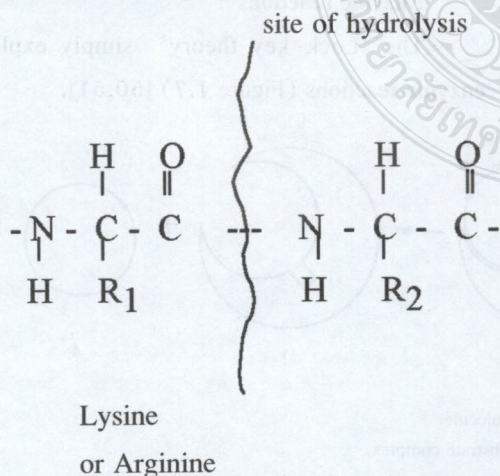
site of hydrolysis

Lysine
or Arginine

Figure 1.9 Specific site of protein hydrolysis by trypsin [50].

Enzymes for degumming

Trypsin, papain and bacterial enzymes are the main types of enzymes for silk degumming. These enzymes are called 'proteases' because they degrade proteins and their degradation products are polypeptides, peptides and other substances by hydrolysis of the -CO-NH- linkage [52]. The proteolytic enzyme action is shown in Figure 1.8.

Carboxylic component   Amino component

Sericin may be less crystalline than fibroin, and it has relatively high lysine and arginine contents. Fibroin may be less affected by trypsin due to its lower proportion of lysine and arginine residues (Tables 1.1 and 1.2).

Papain

Papain enzyme, derived from papyrus latex, is a sulphydryl enzyme which is most active in the range of the pH between 5.0 and 7.5 at 70-90°C. Before the degumming process, papain must be activated by a sulphydryl reagent. Activated papain attacks the peptide bonds between the carboxylic acid group of lysine or arginine and the adjacent amino acid residue. Minor cleavage occurs at the carboxylic acid group of histidine and also of glycine, glutamic acid, glutamine, leucine and tyrosine residues [37].

Bacterial enzymes

A bacterial enzyme, alkalase, produced by Novo [50,53], has been found to be effective in hydrolysing sericin. This bacterial enzyme was claimed to be more effective than trypsin and papain in that it will completely decompose sericin in 1 h at 60°C, pH 9.0 [37].

Other alkaline-stable proteases have been found suitable for silk degumming such as degum mase, esperase, proteinase and sauinase [37,53].

Enzyme degumming has the following advan tages over the conventional degumming with alkaline soap: [53]

1. it has a specific reaction thereby it may give a minimum damage to fibroin,

2. it has a lesser risk of over degumming than alkaline soap degumming,

3. weight loss can be easily modified by adjusting the concentration of enzyme, the reaction time and the use of optimum pH and temperature,

4. with the enzyme method, silk is treated at low temperature (e.g. at 40°C) not only reducing energy costs but also preventing fibre weakness,

5. enzyme treatment is an environmentally friendly process because enzyme can be readily biodegradable in nature [54], and

6. there are no soap required in enzymatic degumming process, therefore, uneven dyeing problem caused by metallic soap can be avoided.

Enzymatic degumming also has some economic disadvantages as:

1. it need some pre-treatment processes, since the gum must be swollen before the enzyme bath [43,55], and

2. it is a very slow reaction compared to alkaline soap degumming [43], on the other hand,

enzymatic degumming may give a better degumming result because it can be well controlled compared with alkaline soap degumming. Therefore, fibroin may be intact.

Methods for determining the efficiency of the degumming process.

There are several methods for assessing the efficiency of the degumming process, such as

1. the gravimetric method [43,56]

2. staining methods with some dyes which distinguish between fibroin and sericin, for example, C.I. Direct Red 2, C.I. Direct blue 22, C.I. Direct Red 61, C.I. Direct Green 9 [37].

3. the degree of fibre damage may be assessed by determining the viscosity of the degumming solution, or the tensile properties and the primary amino group content of the fibre, and

4. the efficiency of degumming may be assessed using the scanning electron microscope (SEM).

The gravimetric method is commonly used in the assessment of the efficiency of degumming [57-59]. The gravimetric method is the most simple, measuring the weight loss of the sample. However, it may not reveal any residual sericin and it does not assess damage to the fibroin. Tensile strength gives more information about damage to the treated sample. SEM examination [50,57,61,62] may be more suitable for revealing fibre damage and the residual sericin.

Unlike the gravimetric method, the staining method is a method to confirm that there is no sericin left on the sample but it cannot assess this quantita tively. The determination of viscosity of degumming solution, and determination of the primary amino group contents of the fibre are more difficult to

interpret and there are a few investigators using these methods.

The tensile strength testing method was not considered to be suitable for the present experiments because the silk samples were uneven because of the domestic reeling process.

After careful considerations, the gravimetric method was chosen to assess the degumming in the present experiments. Some of the degummed fibres were examined in the SEM.

9. Dyeing and finishing silk

9.1 Bleaching

Bleaching of silk is for white and pastel shades only. Degummed mulberry silk is slightly off-white in colour while degummed tussah silk still has a colour because of some sericin, which is stubbornly stuck to the fibroin.

Bleaching can be carried out by reducing and oxidising bleaching agents. Sulphur dioxide, sodium hydrosulphite and sodium sulphoxylates are commonly used reducing agents for bleaching silk. On the other hand, hydrogen peroxide, potassium permanganate, sodium perborate and sodium peroxide are oxidising agents for this purpose [63, 64].

9.2 Dyeing

Like wool, silk is a natural protein fibre. Due to this, the mechanism of dyeing silk is dependent not only on free amino and carboxyl groups but also on phenolic with accessible-OH groups. Because of the slightly cationic character of silk with an isoelectric point at about pH 5.0, it can be dyed by anionic dyes such as acid, metal complexes, reactive and selected direct dyes [65-67]. In contrast, free carboxyl groups can form an ionic bond with cationicc dyes (basic dyes) [68,69].

9.3 Printing

The advantages of silk printed fabric lead to the development of micro fibres, synthetic fibres which emulated the silk fibre. Since silk is a very fine fibre, there is more surface area in a silk fabric compared with fabrics made of other fibres. There fore, silk is often used for printing.

Silk fabric can be printed by three methods:

1. Direct printing
2. Discharge printing
3. Resist printing

Information about these processes, and recipes can be found in refs. 70 and 71.

9.4 Finishing

1. Weighting [72,73]

The degumming process causes a weight loss on silk (e.g. 20-25 %). Weighting process is sometimes used to increase the weight of silk. Silk is treated with a suitable organic or inorganic substance in order to increase the weight. The weighting process improves the drapability of silk, which is a highly appreciated property in the case of dress and garment fabrics.

2. Mechanical finishing [74]

Silk fabrics can be calendered using a two-bowl calendering machine so as to improve handle and appearance.

3. Softeners and lubricants [75]

With the presence of softeners and lubricants, silk enhances its unusual properties. Generally, softener is used in the final stage of wet processing of silk.

4. Flame-retardants [75]

Flame-retardants are used on silk fabric to inhibit pyrolysis reactions. Some flame-retardants are alkyl and aryl phosphates, phosphonates, poly (vinyl or vinylidene halides) latexes, poly (halogena

ted acrylate) latexes, colloidal antimony pentoxide and so on.

5. Crease-recovery finishes [23,55,75]

Easy-care properties of silk are not high compared to synthetic fibres. Therefore, cross-linking agents are used for this purpose. These products either react with one another or crosslink the fibroin backbone to form water insoluble products under the action of a suitable catalyst and heat.

6. Oil and water repellent finishes

Oil and water repellent finishes are applied together or separately on silk. Conventional auxilia ries are waxes, metal acid salt and oxides, proteins and nitrogenous compounds, silicones and fluoroche micals [75]. The fluorochemicals produce a versatile finish. They can use in combination with either wax, pyridinium salts or other types of water repellent resins which give a synergistic effect to improve water repellency.

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