CHAPTER 1

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Silk is considered as the queen of textiles since time immemorial across the world. The origin of natural silk is as old as that of civilization and is referred in legends, scriptures, fables and folklores. In India, silk is mentioned in the ‘Vedas’ the oldest scripture in the world originating beyond 10,000 years B.C. Mention of silk was made in other scriptures also like Ramayana (8000 years B.C) and Mahabharata (4000 years B.C). The first written reference as the finest golden silk of Assam was described in ‘Kautilya’s Arthasastra’ sloka-104 (320 B.C). Kautilya stated that the best type of ‘dukula’ was from Suvarnakundya. This was red as the Sun, soft as the surface of the gem, woven while the threads were very wet in mixed uniform texture. This ‘dukula’ was nothing else than Muga silk of Assam, which is related to the fact, that even today, Muga is woven by wetting the yarn in the weft direction of the fabric. Further evidence proved that ‘dukula’ was Muga silk and that Suvarnakundya was ancient Kamrup from references made in Harchacharit, where it was stated that king Bhaskara Varman of Kamrupa (A.D. 594-650) sent to king Harshavardhana some presents of silks, abhoga umbrella wrapped in dukula cloth (Chaudhury, 1959). From the Vedic age the silk industry has had an adventurous course of evolution, becoming established from time to time. It was only since the early nineteenth century that T.W. Helfer coined the scientific name for Muga silk worm as Antheraea assamensis (Helfer, 1837) generating scientific study on this rare species of silk worm.

The oldest textile silk has survived the test of time because of its unique natural characteristics making it distinctive in this century also. Today there are many other textile fibres, but science is yet to produce another fibre like silk. It is also the strongest natural yarn manufactured into fabric having high moisture absorbency making it
comfortable to the wearer. Silk retains its shape, drapes well, shimmers with a luster all of its own and also has a smooth surface that provides a pleasant feeling against the skin. It is light in weight and supple. Among the various textiles, silk is protein fibres converted to fabrics and considered as a luxury material.

Pure silks are product of the silkworms which feeds on leaves of various food plants, nurtured and processed by mankind. There are 400-500 species of silk producing moths in the world, but only 9 species are commercially reared. However in India 5 species of silk worm varieties are commercially used for fabric production. These silk worms are classified as “wild” or “vanya” varieties, e.g. Muga, Eri, Tasar and the well known “domestic” or “cultivated” varieties, e.g. Bombyx mori. These silkworms produce the valuable bio material the silk protein polymers composed of various amino acids. The domesticated Mulberry silk worm is reared indoors in protected environment and contributes to 99% of Indian silks.

The wild silkworms, Antheraea assamensis Helfer (Lepidoptera: Saturnidae) are reared outdoors in natural conditions, which feeds on the leaves of Som (Machilus bombycina) and Soalu (Litsea polyantha) as well as other secondary host plants producing the Muga silk cocoons in the North Eastern Region of India, particularly in Assam (Chowdhury, 1981; Helfer, 1837). By virtue of the narrow ecological distribution of the food plants, A. assamensis Helfer is confined only to Assam state, hence the name ‘assama’ popularly known as ‘Muga’, an Assamese word meaning the rich amber brown (golden) colour of silk having much commercial value (Naresh et al., 2009). The indigenous golden brown colour is permanent and can neither be bleached easily nor damaged by sunlight or common detergents. These cocoons are converted into yams, woven into fabrics which are highly priced and valuable commodity of the Indian Textile industry. It is a silk with the GI tag of Assam. Muga silk fabrics woven from 100 % Muga silk yarn has a natural appearance and appeal that no other fabrics offer. Muga being a part and parcel of the culture and tradition of this region along with the inherent characteristics has enabled it to create a distinct niche in the domestic market. The demand for soft indigenous golden brown coloured
Muga silk fabrics are also on the increasing trend in the export market (Sarma et al., 2008). However the labour intensive nature, high cost of initial production and subsequent processing makes it very expensive for consumers.

The production of Muga silk begins with the silk worms’ eggs which hatch to larvae and feeds on fresh leaves of Som and Sualu trees. After the fifth stage the mature silk worms are brought indoors and placed on dry twigs to spin cocoons. The process of cocoon production is completed in about 50 days in summer and 150 days in winter. Silkworm fibres are naturally extruded from two silkworm glands as a pair of primary filaments (brin), which are stuck together, with sericin protein that acts like glue to form a bave. The liquid silk solidifies on contact with air. Approximately 500 to 600 meters of Muga filaments makes up a single cocoon. Quite a lot of silkworms are required to produce a meter of silk fabric.

The basic material of silk is a fibrous biopolymer composed of two structurally unique polypeptide proteins, fibroin and sericin. Fibroin content in the cocoon is 70-80% while sericin is 20-30% and also contains secondary ingredients such as waxy matter (0.4-0.8%), carbohydrates (1.2-1.6%), pigments (0.2%) and inorganic matter (0.7%) (Talukdar, 2011). Both sericin and fibroin proteins are composed of practically the same amino acids, however the later being more crystalline and coated by sericin is not accessible during degumming (Fornelli, 1994). It has been reported that the molecular conformation of silk sericin obtained from wild silk is not practically different from that of sericin obtained from Bombyx mori silk. The only difference is that the wild silk sericin is relatively insoluble compared to Bombyx mori, mainly due to chemical interaction between silk sericin and inorganic minor components or tannin contained originally in wild silk cocoons (Corbman, 1983). Another reference also indicated that sericin in wild cocoons does not easily dissolve due to the presence of tannin and the cocoons were not easily cooked (Komatsu, 1980). Degumming of Muga, Tasar, Eri silk required more time and severe conditions as sericin is strongly embedded than compared to Mulberry (Teli et al., 2011). As such sericin is likely to remain in the yarn, which tends to give the fabric a harsh effect. In Muga cocoons
sericin is tenacious so has to be boiled in an alkaline solution for 15-30 minutes and reeled into yarn which is woven into fabrics. Part of the sericin remains in the Muga silk fabric (Chowdhury, 1981).

Sericin is a large complex molecular electrolyte which contains many basic groups (e.g. $-\text{NH}_2$) and many acidic groups (e.g. $-\text{COOH}$) in each molecule. The electric charge in sericin changes, depending on the pH value of the solution. In acidic medium (supply of $\text{H}^+$), the sericin molecule is positively charged and in alkaline medium (supply of $\text{OH}^-$), the sericin molecule is negatively charged. At the iso-electric point of sericin pH 3.8 – 4.2, the electric charge in the sericin molecule is balanced and the effective electric charge become zero, resulting in minimal swelling and solubility of sericin. If the pH is raised, the sericin solubility increases proportionately.

Degumming is based on water solubility and higher alkali sensitivity of the sericin as compared with the fibroin at pH value from 9 to 11.5. Strong alkalis as well as long treatment time may however also attack the fibroin (Kadhar et al., 2008).

Muga silk filaments have been studied and its inherent characteristics have been reported. The moisture regain is 11 %, moisture content is 9.5 %, tenacity is 2.8 grams per denier and elongation is 41.90% (Kariyappa, 2008). Single Muga filament denier is 5 to 5.5 (Talukdar, 2012). Excess moisture increases the elongation of silk, but decreases its tenacity. The fabric produced from this fibre is highly durable so has a high demand in the national and international market (Freddi et al., 1994; Devi et al., 2011). The Differential scanning calorimetric analysis of Muga silk revealed thermal decomposition at 362°C (Talukdar, 2012).

In another study the physical appearance silk has a smooth, soft texture that is not slippery, unlike many synthetic fibres. Silk is one of the strongest natural fibres but decreases up to 20% of its strength when wet. It has a good moisture regain of 11 % (Kadolph et al., 2002). The mechanical parameter like elasticity is moderate to poor. It can be weakened if exposed to too much sunlight. It is also attacked by insects, especially if left undegummed and dirty. Conduction of electricity is poor in silk fibre and thus susceptible to static cling. The inherent characteristics of the
basic raw material along with the processing of the yarn, fabric structure, degumming applied, significantly influences the important characteristics like luster, thickness, weight, softness, compressibility, pliability, drapability, tenacity, durability, thermal insulation, resistance to evaporation, air permeability, water absorption, wicking (capacity to transport absorbed sweat away from the point of absorption), etc. (Potter et al., 1967). In case of silk fabrics the purity of the fibres is an important criteria for experiencing the unique characteristics.

Silk processing from cocoons to the finished clothing articles consists of a series of steps which include: reeling, weaving, degumming, dyeing or printing and finishing. In Muga silk fabric degumming is a process or finish which improves, refines and gives a polished look (Sarma et al., 2008). Fig.1 depicts the factors influencing the pure silk fabric characteristics.

Degumming is the key process during which sericin is totally removed and silk gains the typical shiny effect, soft handle and elegant drape highly appreciated by the consumers (Freddi et al., 2003). Derived from the French word, ‘Degommage’, degumming is the heart of wet processing of silk (Sah, 1993). The sericin is removed but the fibroin must not be damaged (Saligram et al., 1993) by high temperature and highly oxidative environment for extended length of time which has a harsh effect on
the silks. It is one of the processes where chemicals are used in the silk industry. The aesthetic appeal can be improved by better degumming (Krishnaveni et al., 2008).

Removal of sericin percent and correct execution of degumming process has a decisive effect on the aesthetic and wearing qualities of silk like softness of handle, crease resistance, characteristic lustre and smoothness. Scientifically planned, controlled and regulated degumming process would bring in lot of advantages to enhance the performance during conversion of yarn to fabric and also will have an impact on the final quality of finished goods (Reddy et al., 2003).

In the normal course, degumming of silk is done in three different stages. Firstly while the cocoon is cooked to soften the filaments for reeling, a certain portion of the sericin is lost. Later while the raw silk is degummed to make it suitable for the weaving operation and finally while the fabric is subjected to the degumming operation during finishing the rest of the sericin along with other impurities is removed completely from the silk. Being a major component of silk, it has been selectively removed from fibroin during the manufacturing process to make the silk fabric lustrous. But the effectiveness of removing sericin is difficult to assess and prolonged degumming may cause damage and premature termination will result in incomplete removal of sericin (Koshy, 1993).

Mechanism of sericin removal can be described as a combination of dispersion/solubilization and hydrolysis, caused by strong alkaline compounds added to the bath. Therefore, suitable procedures needs to be performed for controlling process parameters, such as temperature, time and salt concentration in order to attain effective sericin removal without triggering the hydrolytic degradation of fibres, which can be easily induced by the presence of harsh chemicals in the treatment bath. Undesirable fibre degradation appears as loss of aesthetic and physical properties, such as drop of tensile strength, surface fibrillation, poor handle, dull appearance (Frank, 2001: Shukla et al., 1992).

Degumming has also been applied for diversification in Mulberry silk yarn by varying the removal of sericin content from 5 to 25 %. Mulberry fabrics made from
ecru silk yarn may have all the sericin intact, for instance the unprocessed Murshidabad silk fabrics has all the sericin, while the fabrics made from souple silk yarns may have only 10% to 15% sericin. On the other hand spun silk contains only about 5% sericin. Along with sericin as the main impurity the silk fabrics may contain sizing agents like starch, gum, tallow etc. The main impurities do not respond to the usual degumming treatments so desizing precedes the degumming (Chopra et.al., 1993).

Several laboratory studies and field tests in recent years have been tried mainly in Mulberry silks and to some extent in Tasar and Eri silks. Past studies on degumming are focused on Mulberry silk and a considerable body of literature is available on this area. Although Muga is a premium silk in India, the research work on pure Muga silk fabric is not significant. Only some products have been developed using Muga silk and scientific data on degumming as well as the improvement of functional properties after degumming are nonexistent.

*Muga* silk fabric is appreciated for its natural golden colour, durability inspite of the many drawbacks in the yarn and fabric structure. The appeal of the fabric depends on the interaction of the visual effect of the texture, shine and characteristics like softness, smoothness, thickness, stiffness, drape etc. in the hands of the consumers with traditional value. These characteristics of the *Muga* silk fabrics can be improved by degumming or biopolishing with natural agents for fetching a wider market.

*Muga* silk fabrics are usually woven with yarns reeled from the *Muga* cocoons of two commercial crops ‘Jethua’ (May-June) and ‘Kotia’ (Oct.-Nov.). Single ply yarns are used in the warp and weft directions of *Muga* fabrics, unlike that of Mulberry silk yarns which are two ply twisted, three ply twisted and processed. However the *Muga* yarns used in the weft are usually higher in denier then the warp yarns. Sizing is applied to the warp yarns to increase the strength for withstanding the stress and strain as well as for overcoming the fibrillations of the yarns which gets caught in the reed during weaving in the handlooms. The production of yarns and fabrics being totally manual the defects occur on the woven fabrics which are camouflaged by applying
sizing over the fabrics while weaving. Besides the demand for *Muga* silk fabrics being higher then the actual production has led to the trend of using look a-like dyed yarns and excessive application of sizing on the fabrics resembling the surface features of pure *Muga* silk fabrics.

The authenticity of the silk fibres in the yarn and fabric was identified visually and with tactile experiences in the absence of any labeling system. However with the implementation of Silk Mark label by Silk Mark Organisation of India (SMOI), Central Silk Board, Ministry of Textiles, Government of India since 2004, has been facilitating identification of 100% pure silk by implementing Silk Mark scheme. The genuine silk producers, manufacturers, dealers registered with SMOI, has been affixing Silk Mark labels on the pure silk products after testing. The tests followed were - flame test, microscopic and solubility tests to identify the purity of Silk. So a detailed study was required for identifying *Muga* silk as the quality of the *Muga* silk fabric depended on the fibres in the web of the fabric. Besides the pure *Muga* silk fabrics with its inherent qualities along with the acquired characteristics while being converted to fabric was required to be studied prior to, as well as after application of the degumming treatments, so that the qualitative and quantitative changes in the degummed *Muga* fabric can be assessed.

In case of *Muga* silk fabric degumming is a refining process consisting of removal of the added reagents, any incidental dirt picked up in any of the operations and sericin. Since all natural and acquired impurities except sericin constitute only a very small fraction and are comparatively easily removed the degumming process is considered primarily as removal of sericin.

Degumming in the presence of soap, alkali, organic acid or synthetic detergents and oxidizing agents under general conditions of treatment such as high alkalinity, high temperature and highly oxidative environment for extended length of time tends to degrade the *Muga* silk fabric leading to undesirable aesthetic and physical properties such as dull appearance, surface fibrillation and tensile strength loss. Biodegradable natural agents can be an alternative to replace soaps, alkalis, organic acids or synthetic...
detergents. Besides these natural agents are also cheap, abundant, eco-friendly and economical.

The challenges facing the textile industry have intensified during the last decade. Current awareness of the negative environmental impact of chemical processing in textile industry, combined with increased strict legislation on industrial effluents, has led to the search for advanced, non-polluting processes, for treating both natural and synthetic fabrics. Enzymes and some natural agents can represent good alternatives for the traditional textile processes allowing reduction of costs, protection of the environment and increasing safety of mankind at the same time contributing to the improvement in quality, enhancing the inherent and functional characteristics of the final products.

The removal of sericin and the changes in the silk fabric after degumming are required to be assessed to understand the changes in the fabric qualitatively as well as quantitatively. Degumming loss in the fabric represents a quantitative evaluation of the degumming efficiency indicating the weight loss (expressed as a percentage of the initial weight). The extent of degumming can be qualitatively assessed by viewing the degummed fabric under the Scanning Electron Microscope. The fibre damage in the fabric can also be assessed by SEM (Gulrajani, 1992). Tensile strength i.e. maximum load (kgf) and elongation at break % assessment are also used for depicting the qualitative change in the degummed fabric sample (Gulrajani et al., 1996; Duran et al., 2007).

The water transport rate is measured with the vertical fabric strip wicking test to find the capability of the fabric to transfer water before and after degumming (Gulrajani et al., 1997). Wickability of the fabrics is a qualitative assessment of the degumming treatment. As liquid transporting and drying rates in fabrics are a vital factor affecting the physiological comfort in garments (Fangueiro et al., 2010). Fabric controls the microclimate, which is the air encompassing the body. In hot climates, how a fabric feels to the wearer is one of the most important attributes. In order to keep the body dry and comfortable, the fabric must be able to transport the moisture away
from the skin either through diffusion or wicking to the surface to evaporate (Simile et al., 2004). Fabrics that rapidly transport moisture/liquid away from the surface of the skin makes wearer feel more comfortable by keeping the skin dry (Yuvarani et al., 2010).

The influence of process conditions on the level and quality of silk degumming has been studied extensively using two factors by the researchers. Reports in the literature provide considerable detail regarding degumming of silk textile but most of the degumming studies were conducted using conventional methods, i.e. investigating a process by varying one factor whilst maintaining all other factors involved at constant levels, such methods are time-consuming and of low efficiency. Box Behnken statistical method is being used to obtain optimum parameters of degumming and the relation between different variables with minimum trials. The Box Behnken design allows reduction of the number of samples and also enables the incorporation of most of the main effects, as well as first order interaction and quadratic relationships (Teli et al., 2011). Response Surface Methodology (RSM) is more advantageous than the traditional single parameter optimization in that it saves time, space and raw material (Sah et al., 2010). It is an effective statistical technique for optimizing complex processes. RSM reduces the number of experimental trials needed to evaluate multiple parameters and their interaction. It is less laborious and time-consuming than other approaches.

In this work, the effect of three process conditions viz. time, temperature, degumming agent concentration being adopted in the silk industry, has been studied for degumming of Muga silk with respect to degumming loss % by using the Box Behnken design software in conjunction with Response surface methodology (RSM) of Design Expert software (version 6.0). An attempt has been made to apply the proteolytic enzyme Papain and other natural products like Reetha, Kolakhar, Crude Papain as natural eco-friendly degumming agents and compare with that of degumming with Na₂CO₃. Box Behnken design was used for developing the experimental design matrix and Response surface methodology (RSM) was applied for analyzing the experimental results to obtain optimum process parameters of degumming and the relation between
different parameters as well as minimise the number of trials.

The thrust of this work is to explore these areas and contribute to the scientific advancement for improvement of *Muga* silk fabric. The goal was to generate information on the characteristics of pure *Muga* silks and degum with different agents with the objectives as stated below:

- To identify the pure *Muga* silk fabrics from the collected fabric samples.
- To assess the physical and functional characteristics of the identified pure *Muga* silk fabrics.
- To degum the selected *Muga* silk fabrics with enzymes, other natural agents and Na₂CO₃.
- To assess the effect of process parameters on degumming loss of *Muga* silk fabric.
- To assess the optimized degummed *Muga* fabric with different agents.